

HYDROGENATION

OF ORGANIC SUBSTANCES

HYDROGENATION OF ORGANIC SUBSTANCES

Including Fats and Fuels

BY

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PREFACE TO THE THIRD EDITION

IN addition to a thorough revision of the material contained in the previous editions, this volume includes several chapters embracing important new developments. These include the hydrogenation of coal and petroleum oils and a very full treatment of the reaction between carbon monoxide and hydrogen with its startling results in the solvent field.

The fundamental importance of the economic utilization of coal, shale, petroleum and other carbonaceous raw materials is reflected in the attention being directed to defining the best working conditions in established high pressure hydrogenation processes, and to improving the equipment, especially the design and construction of apparatus adapted to withstand the high temperatures and increasingly higher pressures used. Improved methods are being sought which will facilitate the separation of the gaseous and liquid products as well as solid residues.

It has seemed fitting to include not only methods of preparation of various hydroaromatic bodies, but also to point out many of their uses. Owing to the enormous number of hydrogenations in this field, the material necessarily has been condensed to a minimum of space. In every case it has been attempted to provide a journal reference which will enable one interested in a particular phase of the subject to consult the original article.

The active development of the hydrogenation of glyceride oils which was so prominent a few years ago has largely subsided and out of the welter of proposals have come a few useful processes which have become well standardized. An equal state of feverish activity is now presented in the development work progressing in the field of high pressure hydrogenation of coal and petroleum oils and also in the production of solvents by the hydrogenation of carbon monoxide. Many years doubtless must elapse before the numerous assertions and findings shall have reached the stage of discard or confirmation. In the chapters relating to hydrogenation of coal and mineral oils and their residues, and of carbon monoxide, the author has made a complete review of the work accomplished to date, in so far as the data are disclosed by publication. Furthermore the text which follows does not overlook the growing importance of hydrogenation as one of the tools of research in connection with the identification of unsaturates of unknown constitutions.

Frequent use has been made of the various abstract journals, such as Chemical Abstracts of the American Chemical Society, and British Chemical Abstracts. The author wishes to express the obligation arising from the utilization of information conveniently derived from such publications. Thanks also are due to those experimentalists in this country and abroad who have furnished data on various

hydrogenations. The author likewise is appreciative of the courtesies extended by Prof. R. T. Haslam and his associates of the scientific staff of the Standard Oil Company (New Jersey) in connection with the subject of petroleum hydrogenolysis.

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C. E.

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HYDROGENATION

CHAPTER I

CATALYTIC HYDROGENATION

INTRODUCTION

100. In strict usage the term hydrogenation is applied only to the reactions in which hydrogen is added to an element or to an unsaturated compound. It is not this limited meaning that has determined the selection of themes for treatment in the present work. To define our subject matter accurately is not easy. Roughly, however, it may be said to cover all cases where molecular hydrogen is made to react with organic substances. Some of these are true hydrogenations, some would strictly be called reductions, while others are dehalogenations. In a few cases, introduced because of their close technical connection with hydrogenations by molecular hydrogen, the hydrogenation of one substance takes place at the expense of the hydrogenation of another.¹

101. The majority of the reactions here described are obviously catalytic. Others, notably the "non-catalytic" forms of berginization, may depend on catalysts which have not been identified.

102. Typical of the class of reactions in which we are interested is the first recorded catalytic hydrogenation of an organic compound. This was the production of methylamine from hydrocyanic acid by passing the vapor of the latter, mixed with hydrogen, over platinum-black.²

103. A few scattered instances of catalytic hydrogenations of organic substances can be culled from the chemical literature of the three decades following Debus' discovery. But they are of minor importance. It was not until 1897 that hydrogenation began to be recognized as one of the major methods of chemical technique. This was due to the brilliant researches of Sabatier and his associates. The work is recorded in a long series of articles, published, for the most part, in the *Comptes rendus* of the Académie des Sciences and in the *Bulletin de la Société Chimique de France*. In a condensed form this work is described in Sabatier's book *La Catalyse en Chimie Organique*.³

104. The result of Sabatier's work has been an astonishing development of catalytic hydrogenation not only in the laboratory but in the industries. The most striking industrial application is to the hydrogenation of fatty oils by the

¹ A number of examples will be found in the chapters on the hydrogenation of mineral oils (XLIX to LI).

² Debus, *Ann.*, 1863, **128**, 200.

³ Translation by Reid: *Catalysis in Organic Chemistry*. Van Nostrand Co., 1922.

catalytic addition of hydrogen at the ethylenic linkages of their acids, with the production of glycerides of saturated (or relatively saturated) fatty acids and a corresponding rise in the melting-point. This process has been applied on a colossal scale for the production of edible and of soap fats.

105. Other applications of major importance are the synthesis of methanol by the catalyzed interaction of hydrogen and carbon monoxide, the hydrogenation of coal and of petroleum.

CATALYSIS

106. Many a chemical reaction which, when the reactants are simply brought into intimate contact, proceeds, if at all, with extreme slowness, may be much accelerated by the introduction of a specific "foreign" substance, although this substance, at the end of the reaction, has, itself, undergone no chemical change. Such a reaction is called catalytic, the accelerating body is named a *catalyst*,⁴ the action of the catalyst is known as *catalysis*.

107. *Early History of Catalytic Chemistry.* Though many industrial methods of high antiquity are now known to depend on catalytic processes, it was not till the end of the eighteenth century that a chemical reaction, belonging to the type which we have learned to call catalytic, was first scientifically investigated. In 1794 Mrs. Fulhame published "An Essay on Combustion," in which she dealt with the influence of water on chemical reaction, more especially in the reduction of metallic oxides and in the oxidation of carbon monoxide, and clearly demonstrated the necessity for the presence of water, at least in traces, for the production of reaction.⁵

108. The subjoined list shows the chronology and the direction of early work on this subject.

- 1794. Fulhame on rôle of water in promoting reactions.
- *1812. Kirchoff discovered that when starch is converted into sugar by the use of dilute acids, the acid remains unaltered.
- 1817. Humphry Davy found that platinum wire at a temperature below red heat caused the combination of oxygen with coal gas, cyanogen, hydrogen cyanide, alcohol and ether.
- *1818. Thénard, having discovered hydrogen peroxide, showed that it was stable in the presence of acids,⁶ but very unstable in alkaline solution, and that decomposition was accelerated by the presence of silver, gold, platinum, the fibrin of clotted blood, and other substances.
- 1818-1819. Erman found that platinum at 50° C. caused the ignition of oxygen and hydrogen mixtures.
- *1820. Edmund Davy, by means of finely divided platinum, oxidized ethyl alcohol to acetic acid.
- *1822. Döbereiner, by use of spongy platinum in the cold, produced combustion of hydrogen in oxygen.
- 1823. Dulong and Thénard extended Döbereiner's observations to gold, silver and glass, above certain temperatures.
- 1831. P. Phillips took out an English patent for producing sulphur trioxide by air oxidation of sulphur dioxide in the presence of platinum sponge.
- *1834. Mitscherlich worked on the rôle of sulphuric acid in the "continuous" process of making ether from alcohol.

⁴ Preferred to the term "catalyzer" because the latter might apply to the apparatus in which the operation is carried out.

⁵ Rideal and Taylor: *Catalysis in Theory and Practice*.

⁶ The first recorded observation of what is now known as negative catalysis. Aqueous solutions are unstable: the decomposition is retarded by acids.

109. In 1835 Berzelius, in a communication to the Swedish Academy of Sciences,⁷ collated those observations which in the foregoing list are marked with an asterisk, and showed that they had a novel characteristic in common. In each instance a body, foreign to the reaction, as judged by the initial and final components of the latter, exhibits the power of inducing "decompositions and different recombinations" of those components, while remaining itself "indifferent." To this kind of action Berzelius applied the name Catalysis.

110. It little matters that Berzelius described this action as "... very different from chemical affinity," or that he announced it as due to a "... new force, which was hitherto unknown—not quite independent of the electrochemical affinities of matter—only a new manifestation of the same ...,"⁸ though he thereby fired the first shot of a long conflict, a war largely of terminology. The cardinal thing that Berzelius pointed out was the existence of a type of chemical reaction which was, at that time, novel, and which seemed exceptional. We now know that catalysis is an extremely frequent phenomenon. If we extend the term, as there is much justification for doing, to the part played by solvents and by radiation it is well-nigh universal.

111. Ostwald has said, in this connection, that there is probably no chemical reaction which cannot be catalyzed and that there is probably no substance, element or compound which cannot serve as a catalyst of some reaction.

112. **Homogeneous and Heterogeneous Catalyses.** A catalytic reaction is classed as homogeneous or as heterogeneous according to whether it takes place in a homogeneous or in a heterogeneous system. A homogeneous system is one, all of whose components are present in the same phase, i.e., all gaseous, or all liquid. A heterogeneous system is one whose components are not all present in the same phase, i.e., they may comprise gas with liquid, or gas with solid, or liquid with solid, or gas and liquid with solid.

113. Thus, when the combination of oxygen with hydrogen is catalyzed by water vapor, all the components are gaseous and the catalysis is said to be homogeneous. So, also, the continuous process of ether manufacture from alcohol by the action of sulphuric acid is a homogeneous catalysis, all the components being in one phase, liquid. When nitromethane vapor, mixed with hydrogen, is passed over nickel at 150°–180° C., methylamine is formed. This is a two-phase heterogeneous catalysis: the reactants are gaseous, the catalyst solid. When hydrogen is bubbled through a fatty oil, containing nickel in suspension, at 180° C., the unsaturated fatty acids are hydrogenated. Here we have a three-phase heterogeneous catalysis: the reactants are a gas and a liquid, the catalyst is a solid.

114. **Autocatalysis.** A reaction which is accelerated by its own products is called autocatalytic:

If pure copper be treated with pure nitric acid, the acid attacks the metal very slowly. But, the reaction once started, the nitrous acid, which is one of its products, accelerates the process and the action becomes violent.

115. In a typical autocatalysis, if the progress of the reaction be plotted, time along the axis of abscissae and amount of product along the axis of ordinates, a characteristic curve results. At first it rises slowly, then more and more

⁷ *Jahresber.*, 1836, 15, 237.

⁸ Quoted from Rideal and Taylor, *loc. cit.*

steeply to a maximum, when it again flattens out as the action gradually dies away. This curve is shown in a pure form if the drying of linseed oil is plotted.

116. Mathews has pointed out the interesting analogy that exists between the behavior of linseed oil undergoing autocatalytic oxidation and the elementary processes of memory.

117. **Negative Catalysis.** An essential property of a catalyst is its acceleration of a reaction. Here the term acceleration is used in its mathematical sense, so that it may be positive or negative. Negative acceleration is, of course, retardation; negative catalysts retard reactions. The majority of catalyses with which the chemist has to deal are positive. Negative catalysis of practical importance is occasionally met with, and this class of action is of considerable theoretical interest.

118. The action of acids in retarding the decomposition of hydrogen peroxide has already been mentioned (para. 108, footnote). Another familiar commercial instance of negative catalysis is the addition of alcohol to chloroform to prevent the formation of carbonyl chloride.

119. The action of substances which check or prevent catalysis is sometimes, intentionally⁹ or by confusion, classed with negative catalyses. It seems better to treat these matters apart, under the usual name of Catalyst Poisons.

120. For facility of exposition, we have, so far, dealt with the nature of catalysis by exemplification rather than by definition. A concise definition, adequate in scope, yet of general acceptability, is required.

121. A definition offered by Ostwald is: "A catalyst is a substance which changes the velocity of a given chemical reaction without modifying the energy factors of the reaction."

122. **Catalysts and the Initiation of Reaction.** This definition involves the tenet that a catalyst can modify the velocity of a reaction, but cannot initiate it. The view has not met with universal acceptance. It means, for instance, that, even in the absence of a catalyst, hydrogen and oxygen mixed at the ordinary temperature, would combine, though very slowly. The proof of the negative of this proposition would, indeed, be difficult to the verge of impossibility. In the first place, what time limit are we to allow before requiring a detectable amount of combination? Secondly, in view of the well-known catalytic influence of the walls of containers, how should we know that water, if formed, was not due to this kind of action?

123. Moreover, it has been observed that hydrogen and oxygen mixtures apparently are stable at 2000 atmospheres pressure.

124. It seems, therefore, that some reactions, capable of catalytic acceleration, will, in the absence of a catalyst, commence and proceed so slowly, if at all, that the change cannot be detected. Such cases are scarcely to be distinguished from cases which are initiated by the catalyst: nor could the distinction, if made, be of any conceivable practical or obvious theoretical importance.

The evidence, as it stands, if it does not prove that a catalyst can sometimes initiate a reaction, suffices, at least, to shift the burden of proof to the shoulders of those who affirm the contrary: which is a disconcertingly legalistic argument to encounter in a scientific discussion.

⁹ E.g., Sabatier (tr. Reid): *Catalysis in Organic Chemistry*, 10.

125. There may be some difficulty in accepting that a catalyst, while contributing no energy to the reaction, can initiate the reaction. Usually the explanation offered is that it overcomes or removes "chemical resistance."¹⁰ Poincaré has said that the mental processes of the English-speaking peoples call for the support of a concrete mechanism. Perhaps, therefore, a mechanical analogy may help. If we place a body on an inclined plane whose slope is just less than the angle of slip, it will remain stationary. But if the plane be oiled the body will slide down, although the lubricant has contributed no energy to the system. This is analogous to the catalytic initiation of a reaction. If the slope of the plane is greater than the angle of slip the lubricant will merely increase the velocity of fall. The position at the end will be the same with or without the lubricant. This is analogous to the mere acceleration of a reaction by a catalyst, without change in the final equilibrium.

126. Catalysts and Equilibrium. Another implication in Ostwald's definition is that a catalyst cannot change the final equilibrium of a reaction.

127. Lemoine worked on the decomposition of hydriodic acid with and without a catalyst. He found ¹¹ that at 350° C., in presence of platinum sponge, the limit was 19 per cent, reached almost instantaneously. Working at the same temperature without a catalyst and under a pressure of 2 atmospheres, practically the same limit of decomposition (18.6 per cent) was attained, but after 250 to 300 hours.

128. Berthelot examined the equilibrium attained in the esterification of ethyl alcohol by acetic acid in the presence and in the absence of traces of mineral acid catalyst, at the ordinary temperature. Starting with equivalent concentrations of alcohol and acetic acid, the limit reached was a conversion of 66 per cent of the alcohol, in each case. With catalyst this was attained in a few hours; without catalyst the limit was reached only after years of contact.¹²

129. On the whole the thesis that a catalyst cannot change the final equilibrium of the reaction has been generally, though not unanimously accepted. Even if a true displacement of equilibrium be theoretically possible,¹³ the experimental evidence is slender, and the majority of supposed instances have received other adequate explanation.

130. Reid passed equimolecular volumes of alcohol and acetic acid over silica gel at 100° C. At this temperature the equilibrium corresponds to about 67 per cent concentration of the ester; yet for long periods a yield of 76 per cent and even more was obtained. Taylor suggests that equilibrium may not be reached in the vapor phase at the same point as in the liquid phase.¹⁴

131. In esterification processes and in the hydrolysis of esters in presence of acid catalysts, there is a shift of the final equilibrium which depends on the amount of the catalyst employed.

¹⁰ "We know that chemical reaction velocity is probably directly proportional to the difference in chemical potential and inversely proportional to the chemical resistance; but we have not yet started on the question of what we mean by chemical resistance and consequently we do not know what really determines the speed of a reaction." (Bancroft.)

¹¹ *Ann. Chim. Phys.*, 1877 (V), **12**, 145.

¹² *Bull. Soc. Chim.*, 1879, **31**, 342.

¹³ See: Pro: Thomson, *Applications of Dynamics to Physics and Chemistry*, 1888, 203, 234; Bancroft, *J. Phys. Chem.*, 1917, **21**, 580; 1918, **22**, 433. Contra: Rideal and Taylor, *loc. cit.*, pp. 18 to 20, and references therein.

¹⁴ First Report of the Committee on Contact Catalysis, 1922, 40-41.

Thus, in the hydrolysis of ethyl acetate, with hydrochloric acid as catalyst, the ratio $\frac{[H_2O][CH_3CO \cdot OC_2H_5]}{[C_2H_5 \cdot OH][CH_3 \cdot COOH]}$ in the final equilibrium, rises steadily with increasing concentrations of hydrochloric acid. Jones and Lapworth attribute this to the formation of a compound between the water and the hydrochloric acid. The discrepancy in the equilibrium equation is approximately adjusted by postulating the presence of $HCl \cdot 2H_2O$.¹⁵

132. Some of the apparent exceptions to the rule that catalysts do not change the final equilibrium are due to false equilibria. There are several ways in which these may be produced. Thus, in catalysis at a solid surface, one of the products of the reaction may "poison" the catalyst, either by combining with it chemically and rendering it inert, or, by being strongly and selectively adsorbed at it, covering it and shutting off the reactants. In each instance the reaction will come to a premature end, the end-point depending on the amount of catalyst used.

133. Amygdalin is a glucoside which, on hydrolysis, yields hydrocyanic acid and a sugar. The natural agent for this hydrolysis is an enzyme, and the equilibrium point for the reaction is known. Platinum-black, which has been called an "inorganic ferment," is also capable of splitting glucosides. With amygdalin the hydrolysis with platinum-black stops very far short of the true equilibrium point. This is due to the well-known "poisoning" effect of hydrocyanic acid on platinum catalysts. If the liquid is ventilated the reaction goes further than in a closed vessel, owing to removal of the poison.¹⁶

134. Importance of Equilibrium Conditions in Industrial Catalysis. When a catalytic process, successful in the laboratory, reaches the stage of industrial application a knowledge of the equilibria of the reactions is invaluable. In the case of contact catalyses in the gas phase this knowledge is essential to economic working, for by it alone can be predicted the available ranges of pressure and temperature. The synthesis of ammonia, the contact sulphuric acid process and the manufacture of hydrogen from water-gas by a contact process are now among the greatest of chemical industries. The economic efficiency of these processes and, from the industrial point of view, their survival is due to the care with which the optimum working conditions have been established. This, in turn, was rendered possible by the accumulation of equilibrium data for the reactions.

135. As a result of his own work on the bromination of hydrocarbons, Merezhkovskii rejects Ostwald's conception of a catalyst. He offers as a general definition: a catalyst for a given reaction is a substance capable of modifying the valences of the reagents, capable of reacting reversibly with the reagents, and capable of having at least two degrees of oxidation.¹⁷

136. Directive Effect of Catalysts. When more than one reaction is possible the relative amount of each which actually takes place depends on various conditions of the experiment. Among important factors having influence in determining the direction mainly taken by such a potentially multiple reaction are: the temperature, the solvent, and the action of a specific catalyst.

¹⁵ Jones and Lapworth, *J. Chem. Soc.*, 1911, **99**, 1427. For alternative explanations see: Taylor, *Catalysis and Catalytic Agents*, 1922, 10.

¹⁶ Neilson, *Am. Jour. Physiology*, 1906, 15.

¹⁷ *Bull. Soc. Chim.*, 1926, **39**, 41; *Chem. Abst.*, 1926, 1937.

137. Sabatier found that at the same temperature, 300°, the vapors of isobutyl alcohol decompose: in the presence of copper, into aldehyde and hydrogen, exclusively; in the presence of alumina, into isobutylene and water, exclusively; in the presence of uranium oxide, both ways, giving at the same time the aldehyde and isobutylene.¹⁸

138. **Solvents as Catalysts.** There is a close analogy if not an identity between the influence of a solvent on a reaction and that of a catalyst. A solvent, by bringing solid reactants into the liquid phase thereby increases the number of molecular collisions, accelerating the reaction though itself remaining chemically unchanged at the end. Again solvents exhibit a directive action on reactions similar to that exerted by catalysts.

139. From water solutions of mercuric chloride potassium iodide precipitates mercuric iodide. But when acetone is used as the solvent potassium chloride is precipitated, because mercuric iodide is soluble in acetone.

140. Were it not for the conspicuous effect of the solvent on the equilibrium the identity would be complete. There is, moreover, a way of considering the phenomena of solvent action and of formulating the data relating to the equilibrium which removes even this difference.

141. It will be recollected that, in ester hydrolysis, the equilibrium end-point varies with varying concentrations of the catalyst (hydrochloric acid), and that the cause seems to be the formation of complexes between the acid and the products of reaction.¹⁹ A similar explanation has been given of the influence of varying concentration of the solvent. "The effect of the medium may be regarded as dual. (1) A catalytic action affecting the two actions of a reversible process equally and having no influence on the final state of equilibrium. (2) A specific action dependent upon the relation of the catalyst to each of the reacting substances."²⁰

142. It can be shown mathematically, on thermodynamic reasoning, that the position of equilibrium is independent of the solvent medium if the latter is without specific action on the reactants, and that the equilibrium constant is independent of the solvent if the concentrations of the reactants are expressed in terms of saturated solutions.

¹⁸ Sabatier (tr. Reid): *Catalysis in Organic Chemistry*, 142.

¹⁹ See para. 131.

²⁰ Van't Hoff, quoted in Rideal and Taylor, *loc. cit.*, pp. 25-27, which should be consulted for the mathematical treatment. Compounds of solvents with solutes are known as solvates; see a note on this subject in *J. Amer. Chem. Soc.*, Golden Jubilee Number, 1926, p. 116.

CHAPTER II

ADSORPTION

200. Adsorption at solid surfaces is the power possessed by solids of holding gases and liquids on their surfaces in extremely thin films.¹ This property is of cardinal importance in contact catalysis. Experts are far from unanimous about the mechanism of contact catalysis, especially about the terminology to be used in describing that mechanism, but all begin with adsorption as a condition precedent of catalytic activity at solid surfaces.

201. Two Kinds of Adsorption. While many adsorptions seem to depend solely on the physical characters, others are conditioned, also, by the chemical nature of the adsorbent and of the adsorbate. Adsorptions of the latter class are conspicuous in catalysis if, indeed, they are not the only kind that we meet in this connection. On the other hand, physical and colloidal chemists have occupied themselves almost exclusively with the former class of adsorptions. Some of the reasons for this are fairly obvious. In the nature of things the second class of adsorptions, those in which chemical constitution plays an important rôle, must, so to speak, seem capricious. The adsorbents of this kind are, as we shall see, highly selective in their action; they are easily influenced by poisons; the reasons for their behavior cannot yet be formulated with the precision to which the better disciplined if less gifted "physical" adsorbents lend themselves.

202. A notable example of almost purely physical adsorption is afforded by Patrick's silica gel. It presents an enormous area per unit of mass (estimated 2,500,000 sq. cm. per gram). It is a powerful adsorbent; as a catalyst it is inert for most reactions.

203. It is to such adsorbents that Freundlich's dictum applies " . . . the physical characters of the adsorbed gas are of far more importance than the specific effect between gas and adsorbent, . . . oftentimes gases are adsorbed in the order of their compressibilities."² Neither of these propositions is true of adsorbents which possess high catalytic activity.

¹ More generally stated: "In a system consisting of two or more phases, and being, therefore, heterogeneous, it is often observed that the concentration of any substance is greater or less at the surface of contact of the phases than it is in the phases themselves. This difference of concentration at the phase boundary is what is known as adsorption." The quotation is from an article on Adsorption by Mathews in *Physiological Reviews*, 1921, 1, No. 4. This paper, unfortunately buried in a periodical of a highly specialized circulation, is most illuminating and should be consulted by all interested in this subject.

² *Kapillarchemie*, 2d edition, 1922, 178, quoted in Taylor: *Colloid Symposium Monograph*, 1923, 105.

204. The preoccupation of physical chemists with adsorptions of the purely physical order resulted in their carrying over to the problems of contact catalysis preconceptions derived from that other field of work and, not infrequently, promulgating dogmatically opinions based on inapplicable analogies. For long the physicists dominated catalytic theory; structural chemistry seemed to be inactivated by their mathematical incantations. The result was to retard the sound development of catalytic theory. In the meantime, however, organic chemists familiarized themselves with the tools of the physical chemists and, in alliance with the latter, have of recent years attacked with a fair measure of success the obscure problem of catalytic mechanism.

205. Before entering on a discussion of catalytic theory it behooves us to review the relevant facts elicited by these researches.

206. Langmuir limits the term adsorption to the combination, by means of unsaturated valences, between a surface and atoms or molecules with which it is in contact. In the case of a gas, this is related, not to its ease of liquefaction, but to the specific chemical character of the gas and of the adsorbing surface. Thus all concentrations not dependent on chemical affinity are removed from the category of adsorptions. This permits of a restatement of the case which brings together the physical and the chemical view of contact catalysis. The chemists admit that specific adsorption is the condition of surface catalysis: the physicists admit that specific adsorption is a chemical phenomenon.

207. **Adsorption at Catalytic Surfaces.** Working with hydrogenation catalysts Taylor, Burns and Gauger made careful quantitative observations on adsorption. Nickel, by far the most important catalyst for hydrogenation, shows strong adsorption capacity for hydrogen, carbon monoxide and ethylene. Copper adsorbs carbon monoxide and ethylene more than it does hydrogen.

208. But although active catalysts show high adsorptive capacity for the reactants, the converse is not invariably true, as is shown in the following table. All the metals noted show measurable adsorptions of the reacting gases in the reactions listed.³

Reaction	Catalysts	Non-catalytic
$\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$	Ni, Co, Fe, Pd.	Cu, Pt.
$2\text{CO} = \text{CO}_2 + \text{C}$	Ni, Co, Fe.	Cu, Pt.
$\text{C}_6\text{H}_6 + 3\text{H}_2 = \text{C}_6\text{H}_{12}$	Ni.	Cu.

At a nickel surface carbon monoxide and hydrogen combine to form methane and water: at a copper surface, though adsorption occurs to an equal extent, no reaction ensues. Copper is an adsorbent for hydrogen and for carbon monoxide, but not a specific catalyst for these gases.

209. Proof of the divergence between the adsorption of gases at catalytic metal surfaces and that by porous inert adsorbents has been obtained by Taylor and Gauger in a study of the adsorption isotherms of hydrogen on catalytic

³ Taylor, *loc. cit.*, p. 16; R. N. Pease, *Jour. Amer. Chem. Soc.*, 1923, **45**, 2299.

nickel. The experimental data are also in good agreement with Langmuir's view that such adsorption layers are seldom, if ever, more than 1 molecule in thickness and that they are determined in many cases by electronic rearrangement of adsorbent and adsorbed gas. A study of the adsorption isotherms of hydrogen on catalytic nickel at temperatures between 20° C. and 305° C. has shown that the nickel surface is already saturated with hydrogen at relatively low gas pressures. At 40-mm. pressure at 25° C. nickel is completely saturated with hydrogen and with increase of pressure up to 760 mm. the quantity of gas adsorbed does not sensibly alter. At 305° C. it requires a pressure of only 275 mm. to saturate the nickel surface completely with hydrogen, higher pressures cause no further adsorption.⁴

210. This saturation at low pressures is not confined to the case of hydrogen on nickel. It is true also of hydrogen on platinum and, in a less degree, of carbon monoxide on platinum.⁵

Similar behavior is shown by hydrogen adsorbed on copper,⁶ and by carbon monoxide on copper.⁷

Earlier work on adsorbents of the non-catalytic type showed that saturation was not attained even at pressures far beyond 760 mm.

211. Heat of Adsorption. Making certain assumptions as to the meaning of the phenomenon exhibited by catalytic nickel of saturation at low pressures, Taylor and Gauger calculated (quite provisionally) the thermal quantity involved in the disruption (and formation) of a nickel-hydrogen surface complex. They arrived at a result of the order of magnitude of 2500 calories per mol of hydrogen adsorbed. The method of calculation was subsequently found to be erroneous:⁸ on recalculation a figure of $15,000 \pm 3,000$ calories was obtained. By another method Rideal arrived at 12,000 calories. A direct determination by Beebe and Taylor, with freshly prepared, highly active nickel, gave a heat of adsorption of 13,500 calories per mol.

212. The order of magnitude of the heat of adsorption of hydrogen at catalytic surfaces is more significant than the actual figures. The heat of liquefaction of hydrogen cannot be much larger than 450 calories.

213. Catalytic Adsorption Chemical. The phenomenon of adsorption at a catalytic surface is, therefore, not one of simple condensation: the magnitude of the heat of adsorption is comparable with that of a mild chemical reaction. This appears to be the final proof that the association between interacting compounds and metal catalyst is definitely chemical in type.⁹

214. Thickness of Adsorbed Layer. Langmuir's theory of a monomolecular adsorbed layer receives strong confirmation from the work of Taylor and his associates. The low gas pressure at which saturation is reached shows that

⁴ Taylor, *Catalysis and Catalytic Agents in Chemical Processes*, *Jour. Franklin Inst.*, July, 1922, 17.

⁵ Pollard, *J. Phys. Chem.*, 1923, **27**, 365.

⁶ Pease, quoted by Taylor, *Colloidal Symposium Monograph*, 1923, 108.

⁷ Jones and Taylor, quoted by Taylor, *loc. cit.*, 109.

⁸ Taylor, *Colloid Symposium Monograph*, 1923, 109.

⁹ Armstrong and Hilditch.

there is no tendency to build up layers of adsorbed molecules (para. 209). The results at the higher temperatures suggest that considerable pressures may be necessary before the surface is covered with a layer even one molecule deep. Evidence to the same effect obtained without the difficulties associated with the definition of the surface is furnished by Iredale,¹⁰ who has investigated the adsorption of methyl acetate on liquid mercury by determining the change of surface tension of mercury with varying partial pressures of the vapor. The following table shows this variation from zero pressure to 227 mm., the saturation pressure at the temperature employed (26° C.).

V.P.	0	19	62	109	137	157	227 mm.
γ	472	444	423	419	418	417	412-370 dynes/sq. cm.

From 62 mm. up to the saturation pressure, there is only a slight variation in surface tension with change in vapor pressure. This points to the attainment of an approximately monomolecular adsorbed layer at less than one-third of the saturated vapor pressure. Iredale has calculated the amount adsorbed at 62 mm. as of the order of 4.5×10^{-8} g. of methyl acetate per square centimeter of mercury. This is equivalent to 0.37×10^{15} molecules per square centimeter or to an area of approximately 27×10^{-16} sq. cm. molecule, which is comparable with that deduced by Langmuir for the area occupied by such esters when oriented at a water surface.¹¹

215. Adsorption of Both Reactants. Pease studied the relation between catalytic activity and adsorptive capacity in the hydrogenation of ethylene in the presence of copper and showed that high adsorption of both gases was associated with high catalytic activity. On suppressing the hydrogen adsorption by partial poisoning with mercury, without serious impairment of the ethylene adsorption, the catalytic activity was suppressed. Adsorption of both reactant gases is necessary to this reaction. Dougherty and Taylor showed the adsorption of benzene vapors by nickel.¹² Those here mentioned and many others which might be cited are all instances of the adsorption of reactant gases. In the section on the theory of catalysis we shall have evidence that the proposition is true of liquid reactants at catalytic surfaces.

216. Effect of Heat Treatment of Catalyst. The following table is illustrative of the effect of heat on the adsorptive capacity of metal catalysts.¹³

Catalyst	Heat Treatment	Adsorption at 0° C. and 760 mm.		Observer
A. Active Cu 100 g.	No heat beyond reduction of oxide at 200° C.	H ₂ 3.70 cc.	C ₂ H ₄ 8.56 cc.	Pease
B.	A heated to 450° C. for 1.5 hours.	1.15 cc.	6.85 cc.	Pease
C. Active Ni 27 g.	Reduction of oxide at 300° C.	35	Beebe
D.	C heated at 400° C. for 4 hours.	16	Beebe

¹⁰ *Phil. Mag.*, 1923, **45**, 1088.

¹¹ Taylor, *loc. cit.*, 111-112.

¹² Taylor, *loc. cit.*, 102.

¹³ Taylor, *loc. cit.*, 104.

217. Taylor's Conception of a Catalytic Surface. It will be noticed that, as occurred in partial poisoning by mercury, the depression of the hydrogen adsorption on catalytic copper by the action of heat on the catalyst is much greater than that of the ethylene adsorption. Taylor explains this as follows: The fraction of the surface capable of adsorbing hydrogen is smaller than that which can hold ethylene. The greater adsorptive force required to adsorb hydrogen is possessed by atoms projecting from the surface and so having a specially high degree of freedom from the influence of neighboring copper atoms. They, therefore, have higher surface energy, and higher vapor pressure. When the metal is heated these atoms distil to positions of less surface energy. These atoms of high surface energy will be most affected by heat treatment: they will be preferred positions of attachment of poisons. This speculation of Taylor's has an important bearing on the mechanism of catalysis.

218. Specificity of Catalytic Adsorption. In quoting a remark of Freundlich on the non-specificity of gas adsorption we mentioned that it did not apply to adsorption by catalytic adsorbents. This can be well illustrated by reference to the preferential combustion of carbon monoxide mixed with hydrogen.

219. An important process for producing hydrogen industrially furnishes a product contaminated with carbon monoxide. It has been found that, on adding oxygen equivalent to the amount of carbon monoxide and passing the mixture over certain oxide catalysts, the carbon monoxide is preferentially oxidized even in the presence of a large excess of hydrogen.

The subjoined table gives the ratio $\frac{\text{adsorption of H}_2}{\text{adsorption of CO}}$ by the oxides named at 760 mm. and -79°C. as determined by Benton.¹⁴

220. For exact comparison with working data, the adsorptions of carbon monoxide at low partial pressures should be compared with those of hydrogen at atmospheric pressure. The results, however, demonstrate the trend towards marked preferential adsorption of carbon monoxide.

Ratio = adsorption CO: adsorption H₂.

Oxide Adsorbent	Hopcalite ¹⁵	MnO ₂	CuO	Co ₂ O ₃	Fe ₂ O ₃	V ₂ O ₅	SiO ₂
Ratio =	33	100	34	19	35	17	28

221. With metal catalysts, the ratios are either unfavorable to preferential combustion of carbon monoxide (nickel and platinum) or only moderately favorable (copper).

Metal = Nickel	Pt black	Copper
Ratio = 0.87 at 184°	3.3 at 100°	12
Result = H ₂ freely consumed.	H ₂ freely consumed.	Fair preferential combustion of CO.

¹⁴ Taylor, *loc. cit.*, p. 106.

¹⁵ Cupric oxide 30, manganese peroxide 50, cobaltic oxide 15, silver oxide 5.

CHAPTER III

THE MECHANISM OF CATALYSIS

300. For many years catalytic theory has been one of the liveliest sectors of the chemico-physical battlefield. The most energetically contested questions have related to the phenomena of catalysis at solid surfaces; the controversies resolved themselves into a dispute as to the nature of adsorption, which seemed to be claimed as exclusively physical by the physicists. Of recent years, however, the chemists have rather tellingly asserted a chemical rationale.

301. "Most authors deal with these (adsorption) compounds as if they were not chemical compounds but physical. This gets them at once into difficulties, for the extreme specificity of the reactions, the cleancut substitutions of one base or acid for another, pointing clearly to a chemical union, remain wholly unexplained. They are forced to fall back on their favorite explanation, namely, that the case is one of specific adsorption and let it go at that. In fact the whole subject at the present time (1921) is a perfect morass, and those who wander in this field with physical adsorption for their lantern climb out of one mudhole only to fall into another."¹

302. The explanations offered of contact catalysis may be divided into two groups, the essentially chemical and the purely physical.

303. Chemical Theory. The essentially chemical theory of catalytic action postulates the formation of compounds in which the catalyst is united to the reactant (or reactants) by chemical affinity, i.e., by the valences. These intermediate compounds, in the conditions of the reaction, are unstable: they break down rapidly into new combinations with regeneration of the catalyst.

304. Physical Theories. The first and once most strongly held of the physical theories is the original adsorption theory. According to this, adsorption is a purely physical phenomenon, not due to chemical affinity, and affords a general explanation of contact catalysis. The great concentration of the reactants at the interface between the catalyst and the surrounding medium produces the acceleration of the reaction. This dogma is now discredited: hardly will the most recalcitrant offer it, in its pure form, as an adequate general explanation of contact catalysis.

305. A second physical theory attributes catalytic action at solid surfaces, and especially the specificity of catalysts, to radiation. This explanation is, of course, entirely compatible with both the essentially chemical and the purely physical theories.

306. The Intermediate Compound Theories. The chemical theory of contact catalysis is generally presented in two forms: the definite intermediate compound theory, and the indefinite intermediate compound theory.

¹ Mathews, *Physiol. Reviews*, 1921, 1, No. 4.

307. For example: Sabatier² holds that hydrogenation with finely divided metals as catalysts "... is easily explained by the assumption of unstable hydrides" on the surfaces of the metals. Referring to this, in the translation of the same work, Bancroft affirms that "... the recent work of Professor Taylor of Princeton shows that no hydride is formed."

308. Notwithstanding the strength of the evidence against the purely physical explanation of adsorption in surface catalysis and in favor of the intermediate compound hypothesis, it is still sometimes urged against the acceptance of the latter that only in rare instances can the intermediate compounds be isolated and that, in most, we cannot even say what intermediate compounds are formed. Is this quite logical? Is it in accordance with our habit of thought when judging evidence in a relatively disinterested fashion?

309. Cases frequently occur in which a death can be clearly shown not to be due to "natural causes" and in which suicide and accident can be excluded with almost equal certainty. Does an intelligent person, in such a case, refuse to accept the reasonable hypothesis of homicide, merely because we can neither tell exactly with what make of weapon the act was committed nor arrest and convict the assassin?

310. Recently a writer has said: "Great progress has been made in this country in the theory of contact catalysis since the importance of adsorption has been recognized."³ We may add: "and most of this progress has been achieved since and largely because of the abandonment of the purely physical (i.e., non-chemical) view of adsorption."

311. The whole passage is worth quoting as showing the position now taken up on this matter by a representative physical chemist whose name has been closely associated with the development and exposition of catalytic theory.

312. Bancroft goes on to say: "The very mysterious phenomenon of the poisoning of the catalyst has been cleared up so far as the general theory is concerned, though there is still some question why a given amount of the poison is necessary in any given case, rather than some other amount. Langmuir's conception of oriented adsorption has already proved its value and is going to be of increasing importance. In Taylor's laboratory, at Princeton University, it has been shown experimentally that nickel splits hydrogen into monatomic, electrically neutral hydrogen, as previously postulated by Langmuir. Bancroft has pointed out that ultra-violet light will do many of the things that a catalyst will do, and that consequently the activation of a substance consists fundamentally in the opening of some bond or contravalence, one of the problems then becoming the determination of what bond it is in any given case. This is Baly's hypothesis made a little more definite; it really inaugurates a new organic chemistry, the chemistry of radicles instead of the chemistry of molecules. The statement that reactions were always between ions was never taken seriously because it was known to be inaccurate. It seems probable, however, that most reactions involve activated molecules, the ions being one class of active substances, and the active forms of the organic molecules being not necessarily charged.

313. Stress has been laid upon the importance of differentiating between the two possible types of contact catalysis. In one case there is an intermediate formation of a definite chemical compound, meaning thereby one which is described by the law of definite and multiple proportions. In the other case there is an intermediate formation of an adsorption complex, or indefinite

² Catalysis in Organic Chemistry (tr. Reid), 165.

³ Bancroft in *J. Amer. Chem. Soc.*, Golden Jubilee Number, 1926, 97.

chemical compound if one prefers that term.⁴ Bray believes that these two types merge insensibly, one into the other, and that there are cases which it is impossible to classify under either head. Whether one can separate the sheep from the goats with accuracy is a debatable point; but the value of the classification does not depend on that. Everybody will agree that it is desirable to distinguish between animals and plants, even though it is not possible to draw a sharp dividing line.

314. Taylor believes that the activating atoms (or molecules) of the catalyst usually occupy only a small fraction of the total surface and are those in the surface which are unsaturated—the extra-lattice atoms—which may be held to the mass of the catalyst by perhaps a single bond.

315. The X-ray examination of metallic hydrogenation catalysts has shown that these catalysts, even when prepared at low temperatures, possess the definite lattice structure of the crystalline material.⁵ A granule of such a catalyst must, therefore, possess, in part, the ordered arrangement of the atoms found in crystalline material. The method of preparation of active material suggests, nevertheless, that the ordered arrangement of the atoms has not been completely attained and that, here and there, on the surface of a partially crystalline material, there are groups of atoms in which the process of crystallization is not complete.

316. The atoms in the plane surface of a cubic crystal of nickel will be practically saturated by the neighboring metal atoms in three dimensions, with the exception that there will be a certain degree of unsaturation towards the gas phase. Atoms in the edges of such a crystal will be one degree less saturated than atoms in the surface, by reason of the fact that they are surrounded to a less degree by nickel atoms. For this reason they will possess stronger attractive force for impinging atoms. This increased attractive force at an edge will be surpassed by that obtaining at a corner.⁶ In the incompletely ordered atoms the attractive force will increase progressively as the degree of saturation by neighboring nickel atoms becomes less and less, . . . the methods of preparation of active catalysts . . . tend to produce arrangements of atoms in which these varying characteristics are multiplied. . . . The less saturated atoms in the catalyst surface will be the preferred positions of attachment of catalyst poisons. Hence the varying ratio of adsorption between poisoned and unpoisoned catalyst.

317. On Taylor's hypothesis, the simultaneous formation of ethylene and of acetaldehyde from ethyl alcohol is due to differently oriented adsorption by atoms of the catalyst held differently on the surface or by differently oriented

⁴ If we are to accept that the union of the constituents of these is brought about through their valences (principal, contra or secondary), i.e., by "chemical affinity," there seems no logical reason for rejecting the term "chemical compound" and no reason, unless of convenience, for using "adsorption complex." Terminology is generally the *ultimum moriens* of an obsolete theory.

⁵ Paras. 339 and 340.

⁶ Reboul, *Compt. rend.*, 1913, **155**, 1227, and Reboul and Luce, *Compt. rend.*, 1921, **173**, 917, found evidence that surface chemical activity is greater on curves than on the flat.

adsorption at different portions of the crystal. Adkins claims that the difference in product is due to a variation in the spacing of the atoms or molecules of the catalysts, and he apparently obtained different alumina catalysts by decomposing compounds of aluminum."⁷

317A. Bourguet, using his special palladium catalyst for low-temperature hydrogenations observes that in the reduction of acetylenes and of acetylenic acids and alcohols, there is an

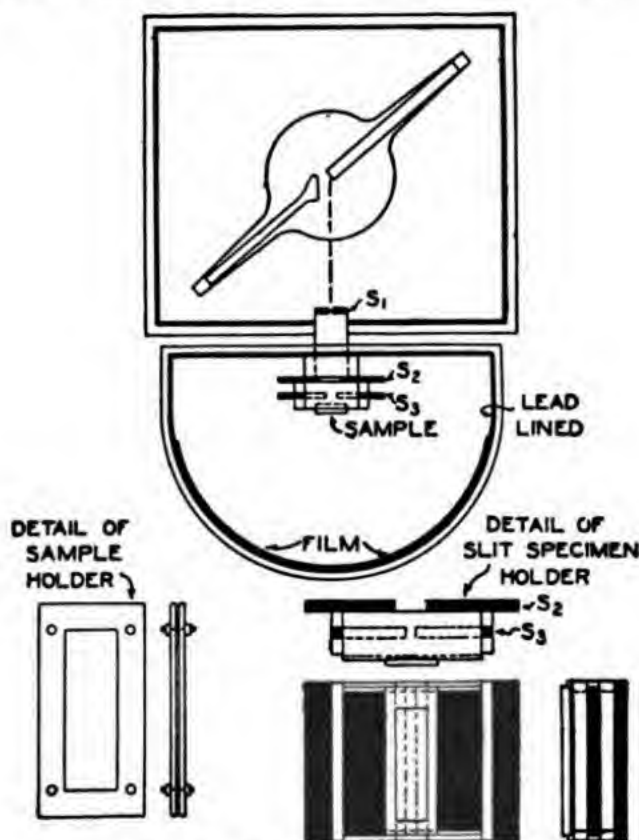


FIG. 1.—POWDER SPECTROGRAPH.

Powder diffraction photographs have been taken by Clark, Asbury and Wick (*J. Amer. Chem. Soc.*, 1925, 2661) of nickel catalysts of widely different hydrogenation and dehydrogenation activities, prepared by reduction with carbon, alcohol, ethyl acetate, hydrogen and sodium hypophosphite. Except for the last, which appeared colloidal, all give identical lines for nickel, $d_{100} = 3.536\text{\AA}$. Hence the difference in activities is not to be ascribed to a difference in lattice type or dimensions.

abrupt change in the rate of reduction when the amount of hydrogen taken up is exactly equal to 2 atoms per mol of the unsaturated compound, and at the same time, and not before, the substance ceases to react with cuprous chloride. In explanation of the results, Armstrong and Hilditch's theory is advocated, a palladium-hydrogen complex being formed first, then adding on the organic substance, and finally decomposing into the metal and reduced compound. As it is observed that in the reduction of a liquid immiscible with water

⁷ Retardation of reaction notwithstanding adsorption of reactants may be explained on the hypothesis of unfavorable orientation. This is held to account for the retarding action of charcoal on the hydrolysis of ethyl acetate. Kruyt and Van Duin, *Rec. Trav. Chim.*, 1921, 2 (4), 249.

the palladium is removed from its aqueous colloidal solution to form a film at the interface of the two liquids, the formation of an oriented layer of the palladium-hydrogen complex is suggested, the hydrogen atoms being directed towards the organic liquid and attracting molecules of the acetylene type in preference to those of the ethylene type.⁸

318. Adkins points out that there are two phases to these catalytic actions which are not necessarily interdependent. The one is the amount of catalyzed reaction which occurs in unit time; this is what we measure when we speak of the "activity" of a catalyst. The other is the ratio of different reactions produced. This is the "specificity" of the catalyst. The activity may (according to Adkins) find its explanation in Taylor's hypothesis. Adkins prefers to attribute the specificity to geometrical relations between the active points, which would determine not only the orientation of the molecule as a whole, but also the strains and constraints to which its parts are subjected. Confirmation of this view is found in recent work of Frolich and his associates (see para. 339). They are able to correlate the variations of specificity of a compound catalyst to variations of the distance separating atoms of the constituent metals. That is, with one distance between the zinc and copper atoms one reaction product is obtained, with another distance a different product. This total effect of molecular polarity causing orientation at the catalyst surface with the strains and constraints due to geometrical distribution of the adsorbing points we may call the *posture in captivity* of the adsorbed reactant molecule (cf., para. 333).

319. Adopting Mathews' apt comparison of adsorption with the act of dressing,⁹ Adkins' hypothesis of the nature of specificity may be illustrated by the facts that to put on trousers one's legs must be free, but a shirt may be donned with both feet fettered. Again the speed of dressing is partly determined by the freedom of one's body and limbs from interference with surrounding objects, which illustrates Taylor's hypothesis and "activity."

320. In summing up the article already quoted Bancroft says: "We must develop a theory of contact catalysis which will enable us to prophesy what catalytic agent will give us a particular result. In the recent synthesis of methanol, we could predict that high pressure would be helpful; but nobody could have said in advance that zinc oxide would be the best catalyst. They had to try one hydrogenating catalyst after another until the right one was found—a slow and unsatisfactory procedure in general. Since the contact catalytic agent activates substances in most cases by opening some bond, we need a study of the organic radicals thus produced, so that we may have a real knowledge of the intermediate steps in organic reactions."

321. A hypothesis is only a scaffolding, usually discarded when the structure is complete, though sometimes it becomes permanently integral with that structure. The hypothesis of the intermediate compound in contact catalysis has, even in its baldest form, been fruitful in suggestion, and, modified by new exact knowledge, promises to be even more fertile in the future.

322. "As far as I am concerned, this idea of temporary unstable intermediate compounds has been the beacon light which has guided all my work on catal-

⁸ *Brit. Chem. Abst.*, 1928, 28A.

⁹ *Physiol. Reviews*, 1921, 1, No. 4.

ysis; its light may, perhaps be dimmed by the glare of lights, as yet unsuspected, which will arise in the better explored field of chemical knowledge. Actually, such as it is, in spite of its imperfections and gaps, the theory appears to us good because it is fertile and permits, in a useful way, to foresee reactions."¹⁰

323. Activation. In discussions on the mechanism of catalysis the expression "activation of molecules" is often used. The acceleration of reaction velocity produced by rise of temperature is a familiar phenomenon and its quantitative expression is known as the thermal coefficient of the reaction. Arrhenius calculated that observed accelerations are many times greater than could be accounted for on purely thermodynamic reasoning. He, therefore, put forward the hypothesis that molecules exist in two degrees of reactivity—activated molecules and inactive molecules, and that an equilibrium is established between these two kinds of molecules, which is definite at each temperature. The effect of a rise in temperature would be to displace the equilibrium so that the proportion of activated molecules would be increased and the reaction correspondingly accelerated. In this Arrhenius made no assumption as to the source of the energy of activation: it is worth while repeating that he had already shown that the source of this energy could not for the most part be caloric due to the rise of temperature.

324. The Radiation Theory of Catalytic Activity. Neither of the intermediate compound theories offers an explanation of the acceleration of reactions by the formation of such intermediate compounds at or on catalytic solid surfaces. They furnish a picture of molecules in a posture adapted for reaction, but no information as to the source of the necessary energy increment. In explanation of the origin of this energy the Radiation Theory was advanced (apparently independently) by Trautz (1906), Lewis,¹¹ and Perrin.¹² This theory does not lend itself to condensed exposition and the reader desirous of understanding the mathematical pros and cons of the matter is referred to the accounts given by Rideal and Taylor¹³ and by Green.¹⁴

325. According to this theory reactions occur between "active"¹⁵ molecules; the increment of energy necessary to activate the molecules being derived from radiation absorbed by or present in the system. This radiation must be of a definite frequency corresponding to absorption bands of the reactant. It is the function of the catalyst to emit radiation of the necessary frequency, thereby displacing to the right the equilibrium:—inactive molecules \rightleftharpoons active molecules, and producing an acceleration of the reaction. If the catalyst, instead of emitting the necessary radiation, absorbs it, the equilibrium is displaced to the left and we have negative catalysis. Neither the experimental evidence nor the mathematical discussion has yet led to a definite acceptance or to a final rejection of this theory: the trend is, perhaps, somewhat favorable. It

¹⁰ Sabatier (tr. Reid), *Catalysis in Organic Chemistry*, 180.

¹¹ *J. Chem. Soc.*, 1916, 109, 796.

¹² *Ann. Phys.*, 1919, 11, 5.

¹³ *Catalysis in Theory and Practice*; 2d edition, pp. 28 *et seq.*

¹⁴ *Industrial Catalysis*, 1928, pp. 94 *et seq.*

¹⁵ See para. 323.

fits in neatly with Langmuir's view of adsorption and its rôle in catalysis at solid surfaces.¹⁶

326. The "Dislocation" Theory. Böeseken is somewhat of a "last-ditcher" in the matter of catalytic theory. According to him¹⁷ consideration of several cases of the Friedel-Crafts reaction leads to the conclusion that the catalyst acts, not by virtue of, but despite the formation of intermediate compounds. The catalyst acts by activating the reacting material and different catalysts may activate the same substance in different ways, producing specific "dislocations" or temporary polarities by a kind of induction. In physical catalysis the effect is produced rather by alterations in the entropy of the system than by considerable changes in the energy of activation; in chemical catalysis the energy factor is the more important.

327. Summary. The present position of the theory of catalysis at solid surfaces seems to be this:—There is general agreement that catalysis at solid surfaces is dependent on adsorption: adsorption of this kind is due to union by valences and is therefore a chemical phenomenon. Most writers hold that the resulting compound is of continuously varying composition, i.e., it is an indefinite chemical compound, otherwise termed an adsorption complex. The high selectivity of solid catalysts may find its explanation in the geometric pattern of the distribution on the catalyst surface of active points (relatively free from interlocking attraction of adjacent atoms) which, combined with polar orientation of reactant molecules on the surface, determines the posture of the captive molecule in such a manner as to expose it to specifically effective bombardment. The radiation theory offers, although tentatively and subject to many reservations, an explanation of the source of the energy increment which causes the indirect reaction, by way of the intermediate compound, to have a higher velocity than the direct reaction.

327A. When the foregoing paragraph was already in type there appeared a number of interesting articles on the mechanism of surface (contact) catalysis. Berthoud (*J. Chim. phys.*, 1929, **26**, 120; *Brit. Chem. Abst.*, 1929, 519A) holds that the introduction of a small amount of a foreign substance into a chemical system cannot bring about a change in the concentration of the active molecules. Even if such a change is assumed it does not follow that the rate of the chemical reaction will be accelerated.

327B. Assuming the existence of active centers on a catalyst surface, Balandin (*Z. Physikal. Chem.*, 1929, **B**, **2**, 289; *Brit. Chem. Abst.*, 1929, 519A) points out that, if all the centers attract by preference the same part of the molecule, there will be no tendency for the molecule to be broken up, and adsorption without reaction will occur. On the other hand, if there are present various types of centers, some attracting one part of the molecule and some attracting another part, decomposition becomes possible. For actual fission to take place, how-

¹⁶ Cf. Green, *loc. cit.*, pp. 97-98. International Critical Tables, vol. 5, pp. 331-334, contain the infra-red absorption spectra of several hundred pure organic compounds and of a large number of natural mixtures, such as oils.

¹⁷ *Chem. Weekblad*, 1928, **25**, 135.

ever, the different centers must not be too remote from each other, but should rather be arranged in groups, each group containing one or more centers of each type, and for such groups the term "multiplets" is proposed. Since catalyzed reactions usually involve a synthesis as well as a decomposition, it is suggested that some centers may simultaneously attract two or more parts of the same molecule, or the same part of several molecules, and if decomposition occurs cause these fragments to unite by directing their valencies one to another. Thus in the reaction $C_2H_5 \cdot OH = C_2H_4 + H_2O$ it may be supposed that active centers of one kind preferentially attract the carbon atoms of $\cdot CH_2 \cdot CH_2 \cdot$ groups, while those of another kind attract both hydrogen and hydroxyl oxygen, which then unite to form water. If a foreign substance is adsorbed by one kind of center only, leaving the others free, the surface will be largely poisoned without its adsorptive power being very much affected, whereas a substance which is able to give rise to active centers of a type in which the surface is deficient will act as a promoter. Balandin thinks it probable that the groups of active centers are densely packed, constituting small surface elements which are to be identified with crystallization nuclei. If it is assumed that the arrangement of centers must be such as to correspond with the symmetry of the molecule in order for reaction to take place, it becomes possible to predict what kind of crystal lattice will catalyze a particular reaction and to calculate the extreme values of the distance between the various centers in order for the attractions to be great enough to dismember the molecule. In this way the theory becomes capable of accounting for many of the observations made in investigations of the catalytic hydrogenation and dehydrogenation of organic compounds.

327C. Storch (*J. Physical Chem.*, 1929, **33**, 456; *Brit. Chem. Abst.*, 1929, 519A) suggests that the function of intermediate compounds in gas-phase catalysis is to provide a complex, containing reactants and catalyst, of a sufficiently large number of degrees of freedom, so that the energy of these may be available for contribution to the energy of activation. The decomposition of hydrogen iodide at the surface of platinum, the catalytic effect of water vapor, and catalysis by gaseous ions are discussed in the light of this extension of the intermediate-compound theory.

327D. Schwab and Pietsch (*Z. physikal. Chem.*, 1928, **B**, **1**, 385; *ibid.*, 1929, **B**, **2**, 262; *Z. Elektrochem.*, 1929, **35**, 135; *Brit. Chem. Abst.*, 1929, 519A) have evolved a theory of the surface catalysis of gas reactions which they believe covers all that Langmuir's theory of a unimolecular adsorbed film and of reaction at a homogeneous surface and Taylor's theory of "active centers" achieve together. For this purpose, it is suggested that the centers of reaction are not distributed over the whole surface, or located at "active points," but rather lie on lines which are phase boundaries. The adsorbed molecules are assumed to be free to move over the surface, but they also undergo "adlineation," i.e., they crowd together at phase boundary lines in the surface in the same way as molecules in free space crowd together at a surface where they are adsorbed. By applying the methods of the kinetic theory it is possible to deduce an expression for the number of

molecules adsorbed on the surface which impinge on unit length of a line in unit time, and this in its turn leads to the "adlineation isotherm." The same equations may be arrived at from thermodynamical considerations, which also afford a proof of the Langmuir adsorption isotherm. By means of the new system of equations, formulæ for the velocities of the various types of gas reactions have been derived, and as these prove to be of the same form as those which are applicable to reactions at bounding surfaces, the new assumption as to the seat of reaction appears to be justified, and may, according to its authors, be regarded as the basis of a truly comprehensive theory of surface catalysis. Eisner's work on the adsorption of heavy metal ions on the edges of crystals (e.g., on crocoisite) and not on the whole surface is adduced as evidence in support of this theory of contact catalysis.

328. A Nickel Hydride.¹⁸ Anhydrous nickel chloride, on treatment with an ethereal solution of a Grignard reagent such as magnesium phenyl bromide, reacts rapidly, forming a dark brown sol containing nickel in colloidal solution. This solution absorbs hydrogen readily, the nickel being precipitated as a flocculent, deep black sediment leaving a clear solution. Measurement of the volume of hydrogen absorbed indicates that a compound of the formula NiH_4 is formed, but on separating the black product and drying it in a current of hydrogen it was found to possess exactly the formula NiH_2 . On treatment with alcohol, the black precipitate at once begins to evolve hydrogen, although it is quite stable in contact with ether. This is accepted as further evidence that the usual processes of catalytic reduction in presence of nickel are essentially chemical, due to the formation of nickel hydride and are not merely adsorption phenomena.¹⁹

329. Kubota and Yoshikawa²⁰ believe that the active, unstable hydrides in reduced nickel catalysts may be divided into three classes: the first and most active is able to hydrogenate benzene, to be poisoned by thiophene; the second can reduce ethylenic groups and is poisoned by ethyl sulphide; and the third is only able to reduce nitro-groups and is poisoned only by hydrogen sulphide.

330. Activation of Gases by Adsorption. Taylor and Kistiakovski²¹ attribute the activation of part of the adsorbed gas in hydrogenation reactions to the action of the unsatisfied valencies of the outlying atoms on the solid surface. They made measurements of the heats of adsorption of small quantities of gas on catalytic surfaces. The curves showing the relation of the heat of adsorption to the degree of saturation of the surface were of different types for hydrogen adsorbed on active copper and on a copper surface poisoned with oxygen and for carbon monoxide adsorbed on active copper. The theory of catalytic surfaces, employed in conjunction with Langmuir's theory of adsorption, is capable of explaining these three types of curve, if it is assumed that only part of the surface atoms can activate the adsorbed gas molecules and that the activation is endothermic.²²

¹⁸ Schlenck and Weichselfelder, *Ber.*, 1923, 56B, 2230.

¹⁹ *J. Chem. Soc. Abstr.*, 1924, ii, 189. For further evidence of the rôle of nickel hydride in hydrogenation see Weichselfelder and Kossodo, *Ber.*, 1929, 62B, 769; *Brit. Chem. Abst.*, 1929, 665A. Hydrides of sodium, potassium, rubidium, caesium, calcium, strontium, lithium, and barium, have been proposed for catalysts in the hydrogenation of hydrocarbons or coal tars (French Pat. 649,976, Feb. 27, 1928, to Hugel, Paul and Boishel; *Chem. Abst.*, 1929, 23, 3060).

²⁰ *Sci. Papers, Inst. Phys. Chem. Res.*, 1925, 3, 223, quoted from Reid, *J. Phys. Chem.*, Aug., 1927, 1141.

²¹ *Z. physik. Chem.*, 1927, 125, 341.

²² *Brit. Chem. Abst.*, 1927, 426A.

331. Activation of Hydrogen "Catalysis at a Distance." When hydrogen at low pressure (3 mm.) is passed over hot palladium, iron, or nickel, and then meets a stream of air from a capillary, a violet luminescence is seen and heat is evolved, or a hydrogen flame burns in excess of oxygen. The effect is most marked with palladium as the activating catalyst.²³

332. Atomic Hydrogen. Wood²⁴ produced atomic hydrogen and showed that it was capable of converting an unsaturated glyceride into a solid fat.

Wartenberg and Schultze²⁵ mixed atomic hydrogen with hydrocarbons (in a Dewar flask). The products were frozen out for analysis at -189° to -193° . Ethylene was the only hydrocarbon which was hydrogenated.

333. Lowering of Heat of Activation. To explain the lowering of the heat of activation of a reaction by a catalytic surface, Burk²⁶ postulates the partial breaking down of a molecule by adsorption at two or more points. In a molecule A·B, the partial separation of A and B would be accomplished by both atoms being attached to the surface, the adsorbing atoms being so spaced that the distance between their points of maximum attraction intensity is not quite the same as the corresponding distance in the molecule A·B.

334. Area of Surface of Catalytic Particles. The measurement of catalytic particle surface and the relation between that dimension and catalytic activity was undertaken for platinum by Levi and Haardt.²⁷ The determination of particle size (and hence area) was made by X-ray method, which was found to be as accurate for such particles as is the ultramicroscopic method for colloid particles. Variation in particle size was attained by heating to different temperatures. From the weight of catalyst used, the particle size and the particle surface area, the whole catalyst area was calculated. This was collated with the activity shown and it was found that, other things being equal, catalytic activity was predominantly a function of total surface but that there was an upper limit. In the case of the decomposition of hydrogen peroxide in presence of a platinum catalyst, with 0.01 g. Pt and 50 cc. of dilute H_2O_2 (5-6 g. to 1000 cc.) this upper limit was a surface of 3000 sq. cm.

335. Measurement of Surface of Film Catalysts. A nickel film, electrolytically deposited on a china clay rod coated with graphite, was activated by oxidation in air and reduction by hydrogen at 520° . The surface area per unit mass was calculated from the slope of the straight line obtained on plotting the conductivity against the equivalent air thickness corresponding with the color shown by the partly oxidized rod. The results show that the surface of electrolytic nickel is 1.84 times the apparent area, and that the apparent surface may be considerably increased by reduction at 400° .²⁸

336. Bowden and Rideal²⁹ have measured the accessible areas of silver platinum, carbon, and nickel cathode surfaces by measurement of the amount

²³ Polyakov, *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 847; *Chem. Abst.*, 1928, **22**, 3338; preliminary note in *Naturwissenschaften*, 1927, **15**, 539; *Chem. Abst.*, 1927, **21**, 3012.

²⁴ *Proc. Roy. Soc.*, 1923, **102A**, 1, quoted by Taylor in *The Chemical Reactions of Hydrogen Atoms*, *J. Am. Chem. Soc.*, 1926, **48**, 2840.

²⁵ *Z. physik. Chem.*, 1929, Abt. B2, 1; *Chem. Abst.*, 1929, **23**, 1867.

²⁶ *J. Phys. Chem.*, 1926, **30**, 1134. Cf. para. 318.

²⁷ *Gazz. chim. ital.*, 1926, **56**, 424; *Chem. Abst.*, 1926, **20**, 3624.

²⁸ *Brit. Chem. Abst.*, 1928, 27. The theory of the method is expounded and details of experimental technique given by Constable in *Proc. Roy. Soc.* 1928, A, **119**, 196-201 and 202-213. For the great difference in area that may exist between surfaces apparently alike, e.g., otherwise similar glass surfaces: (1) washed with acid and water; (2) fire polished, i.e., surface fused and cooled, see Latham, *J. Am. Chem. Soc.*, 1928, **50**, 2987; also Bowden and Rideal, next paragraph.

²⁹ *Proc. Roy. Soc.*, 1928, A**120**, 80.

of deposited hydrogen required to raise the potential by a definite increment, and a comparison has been made of the catalytic activities of these surfaces by observation of the rate of hydrogen evolution. The effects of amalgamation and of treatment of the surfaces by alternate oxidation and reduction, annealing, etching with acid, electroplating, sandpapering, and rolling have been studied. The accessible area of bright platinum is about twice while that of platinized platinum is about 2000 times its apparent area. If, however, the platinum is deposited on a mercury surface, the area is sensibly the same as that of mercury. The accessible area of a sand-papered metal is about 10 times its apparent area, and in the case of nickel, activation by alternate oxidation and reduction causes an increase of nearly fivefold. Cold rolling reduces the accessible area. The specific catalytic activities of the various metals for the electro-deposition of hydrogen are found to differ very widely, but for any one metal the specific activity of the surfaces shows only small variations with chemical or thermal treatment. The effect of alternate oxidation and reduction is chiefly to increase the accessible area by altering the grain size. Violent mechanical treatment, however, although it increases the surface to a much smaller extent, increases the proportion of surface atoms which are out of the crystal lattice and are catalytically the most active. The increase of activity gradually diminishes with aging of the cathode.³⁰

337. Relation of Catalyst Area and Speed of Hydrogenation. This has been examined by Jozsa,³¹ who finds that the velocity of hydrogenation of neutral sunflower oil increased with concentration of catalyst for all the concentrations used (1-10 per cent). There is no apparent relation between the reaction rate and the surface area of the catalyst, determined by Mitscherlich's method. When catalysts are prepared in different ways, it is improbable that, for catalysts with equal nickel content, the amount of active nickel present will be the same. In order to overcome this difficulty, a single catalyst was used, but its surface was varied by using it in conjunction with different carriers. A definite quantity of nickel formate was added to the oil, and 2 per cent of active charcoal. Experiments were carried out to show that the charcoal acted only as a carrier, the catalyst being distributed over its surface. The carriers used comprised active charcoal, two varieties of animal charcoal, blood charcoal, infusorial earth, wood charcoal, and pumice. It was found that the velocity of reaction was proportional to the surface area of the catalyst, so that the value of a catalyst can be found by determining its surface area.³²

338. X-ray Studies of Catalytically Active Metals.³³ Platinum, palladium and nickel surfaces were prepared with the glow-discharge in low pressures of hydro-

³⁰ *Brit. Chem. Abst.*, 1928, 1088A. In *Nature*, 1928, 122, 647, Bowden gives a short account of this work.

³¹ *Z. angew. Chem.*, 1928, 41, 767.

³² *Brit. Chem. Abst.*, 1928, 646B.

³³ Bredig and Allolio, *Z. physik. Chem.*, 1927, 126, 41; *Chem. Abst.*, 1927, 21, 2204. Some interesting observations have been made by Clark, Asbury and Wick (*J. Amer. Chem. Soc.*, 1925, 2661) on nickel catalysts by means of X-ray powder diffraction. Catalysts were made by reduction of various nickel oxides in hydrogen, in methyl alcohol, in ethyl acetate, and also by means of carbon. In one case a nickel powder was prepared by reduction of a nickel salt

of deposited hydrogen required to raise the potential by a definite increment, and a comparison has been made of the catalytic activities of these surfaces by observation of the rate of hydrogen evolution. The effects of amalgamation and of treatment of the surfaces by alternate oxidation and reduction, annealing, etching with acid, electroplating, sandpapering, and rolling have been studied. The accessible area of bright platinum is about twice while that of platinized platinum is about 2000 times its apparent area. If, however, the platinum is deposited on a mercury surface, the area is sensibly the same as that of mercury. The accessible area of a sand-papered metal is about 10 times its apparent area, and in the case of nickel, activation by alternate oxidation and reduction causes an increase of nearly fivefold. Cold rolling reduces the accessible area. The specific catalytic activities of the various metals for the electro-deposition of hydrogen are found to differ very widely, but for any one metal the specific activity of the surfaces shows only small variations with chemical or thermal treatment. The effect of alternate oxidation and reduction is chiefly to increase the accessible area by altering the grain size. Violent mechanical treatment, however, although it increases the surface to a much smaller extent, increases the proportion of surface atoms which are out of the crystal lattice and are catalytically the most active. The increase of activity gradually diminishes with aging of the cathode.³⁰

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³³ Bredig and Allolio, *Z. physik. Chem.*, 1927, 126, 41; *Chem. Abst.*, 1927, 21, 2204. Some interesting observations have been made by Clark, Asbury and Wick (*J. Amer. Chem. Soc.*, 1925, 2661) on nickel catalysts by means of X-ray powder diffraction. Catalysts were made by reduction of various nickel oxides in hydrogen, in methyl alcohol, in ethyl acetate, and also by means of carbon. In one case a nickel powder was prepared by reduction of a nickel salt

gen. They were all inactive for the hydrogenation of ethylene. When oxygen is substituted for hydrogen in the preparation of the platinum and palladium, surfaces of high catalytic activity were obtained. The X-rays show only difference of particle size between these surfaces of varying activity.



FIG. 2.

Clark, Asbury and Wick (*J. Amer. Chem. Soc.*, 1929, 2661) have employed an ingenious method of interpretation of X-ray photographs of nickel powder catalysts. Precision photodensitometer curves from the films were prepared and used to measure relative intensities and widths of lines. The intensities for all were found to be approximately the same and in fair agreement with the calculated values for a face-centered lattice.

339. Frolich, Davidson and Fenske have made X-ray examination of methanol catalysts composed of copper and zinc. The catalysts were shown to be definitely crystalline, with the individual crystal structure of the two components. The unit cell size of each constituent is strongly affected by the presence of the other. Definite relation was established between the nature of the reaction product (specific catalytic effect) and the distance between the atoms of the two components (*cf.*, para. 318). Reduction (partial) of zinc oxide to metal was confirmed ³⁴ (*cf.*, para. 5324).

340. Artificial Preparation of Specifically Selective Catalysts. Rosenmund and others ³⁵ in a series of interesting articles discuss the problem of adding, to a catalytic reaction mixture, a substance capable of influencing the direction (and hence the yield) of the reaction. They succeeded in solving this problem in specific cases. Thus, using palladinized barium sulphate catalyst, pure benzoyl chloride dissolved in pure boiling benzene, toluene or cumene, on passing hydrogen yielded a scarcely weighable amount of benzaldehyde. But on the addition of any of certain substances the yield was greatly increased. The maximum yield was obtained by the addition of "sulphured" quinoline, i.e., quinoline refluxed for five or seven hours with one-sixth of its weight of sulphur. The reaction stopped at the aldehyde stage. Next the

by means of hypophosphite. (See para. 1175.) Certain investigators have endeavored to explain the differences existing in the behavior of nickel catalysts by a fundamental difference in the crystal structure of the nickel. Thus Adkins and Lazier explain the difference between a hydrogen-reduced and an alcohol-reduced catalyst as a change in "the resultant distribution of nickel atoms." The measurements made by Clark, Asbury and Wick show conclusively that the structure of these catalysts, as well as those prepared by reduction with hydrogen and carbon, and by mechanical pulverization, is the same, each having a face-centered cubic lattice of exactly the same dimensions. Differences in activity are not to be ascribed, therefore, to differences in the type or dimensions of the crystal lattice.

³⁴ *Ind. Eng. Chem.*, 1929, **21**, 109.

³⁵ Rosenmund and Zetzsche, *Ber.*, 1921, **54**, B, 435; *Ber.*, 1921, **54**, B, 1092; *Ber.*, 1921, **54**, B, 2033; *Idem* and Heise, *Ber.*, 1921, **54**, B, 638; *Ber.*, 1921, **54**, B, 2038; *J. Chem. Soc.*, 1920, A, ii, 320, 393, 631; 392, 631; *Chem. Abst.*, 1921, **15**, 2435.

reaction was made to give mainly benzyl alcohol, as the result of working in boiling xylene and adding minute quantities of quinoline. By a suitable balancing of the actions of toluene and xanthone, the ester is the main product, without hydrocarbon formation.

An interesting discussion on the bearing of this work on the mechanism of contact catalysis is well abstracted in the references given. The general view is in close agreement with that expressed by Armstrong and Hilditch, viz., that a labile complex is formed of all the reactants and the catalyst.

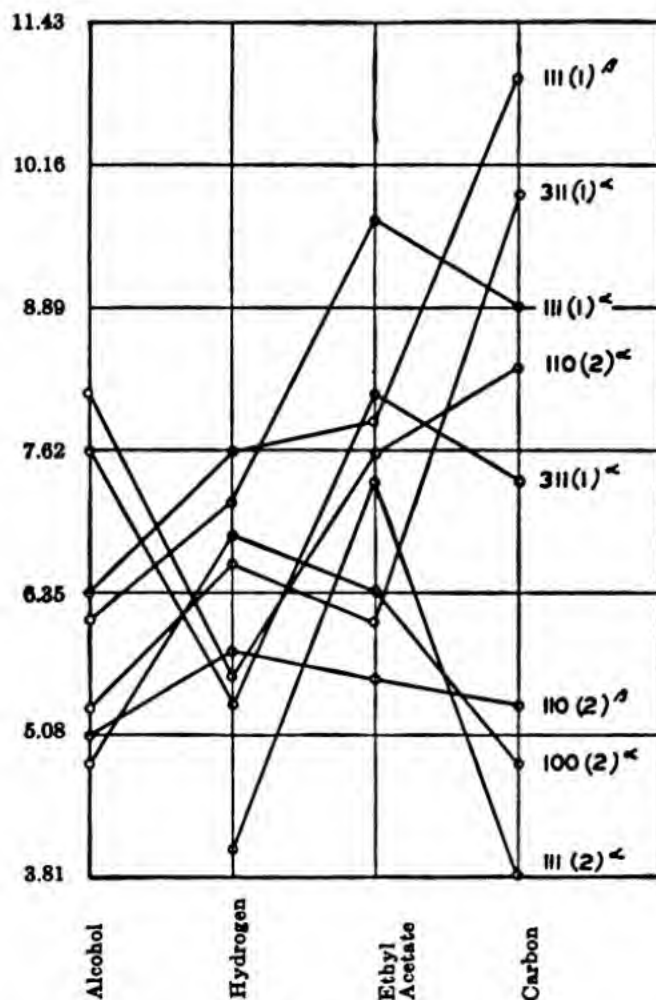


FIG. 3.

The X-ray method employed by Clark, Asbury and Wick (*J. Amer. Chem. Soc.*, 1925, 2661) does not reveal the condition of the surface of nickel catalysts. Such catalysts do not obey the Debye-Scherrer equation connecting line width with particle size, defined for colloidal dimensions. A rough parallelism is found between decreasing line width and increasing catalytic activity.

341. Mittasch³⁴ in an article of general character reviews the history and the position of contact catalysis in 1926, both theoretical and practical. He sees no distinction which can be made between adsorption at a catalytic surface and intermediate compound formation and holds that understanding of surface catalysis will come from better knowledge of atomic and molecular structure and of reaction kinetics.

³⁴ *Rev.* 1926, 59B, 13; *Chem. Abst.*, 1926, 20, 1164.

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²⁷ *Brit. Chem. Abst.*, 1928, 718A.²⁸ *Brit. Chem. Abst.*, 1928, 718A.

catalyst surface. The conclusion was that only certain parts of the surface are apt for the catalysis of the reaction $\text{H}_2\text{CO}_2 = \text{CO} + \text{H}_2\text{O}$.

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⁴⁰ *Brit. Chem. Abst.*, 1928, 150A.

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CHAPTER IV

CONDITIONS OF HYDROGENATION

TEMPERATURE

400. For each compound there usually exists a well-defined range of temperature within which hydrogen is effectively added. Somewhere in this temperature interval lies the mean effective temperature, that is the temperature of maximum saturation velocity. For a number of fatty oils this approximates 180° C. or 356° F. with a nickel catalyst. As a rule hydrogenation is accelerated by a given temperature rise from below the mean effective temperature more than it is retarded by the same temperature increase above this point. In operation on the large scale it is, therefore, better to err by maintaining the oil slightly above rather than below the mean effective temperature, unless of course a lower temperature is prescribed because of the character of the oil. Rapidity of treatment often is desired especially in edible oils where protracted contact with the catalyst introduces the danger of solution of the metallic material in the oil to an objectionable degree. The range of temperature mentioned above varies with each type of catalyst. Platinum and palladium may be used between room temperature and 100° C.; nickel between 150° C. and 200° C.; nickel oxide and copper at about 200° C. and upwards, depending on the physical and chemical constitution of the catalyst.¹

401. Within certain limits the hydrogenation reaction has a considerable normal temperature coefficient as is shown in Maxted's tables in para. 403. But there is occasionally manifested an increase in reaction velocity, caused by increasing the operating temperature, which is in excess of the normal. This finds its explanation in the removal from the catalyst surface of adsorbed temporary poisons. The temperature coefficient of a hydrogenation poisoned by a temporary poison will be abnormally high.² Eventually, a temperature may be reached at which the poisonous product will remain on the catalyst surface only the length of time that is taken up by the completion of the catalyzed reaction of which it is a product. In other words it will no longer retard the reaction. There are many instances which exhibit this temporary poisoning diminishing with increase of temperature. One that has been carefully studied

¹ Ipatiev (*Chem. Ztg.*, 1914, 374) noted commencement of hydrogenation of fatty acids with nickel at 150° C. and with nickel oxide at 230° C. Others have obtained hydrogenation with nickel at much lower temperatures. See Maxted's tables, para. 403 for glycerides.

² Lewis, *J. Chem. Soc.*, 1919, 115, 182.

is reported in the paper by Dougherty and Taylor,³ referred to in para. 722. Carbon monoxide had a strong poisoning effect on the vapor phase hydrogenation of benzene over nickel at 100° C., but the effect greatly diminished as the temperature was raised.⁴

402. In respect of the hydrogenation of fatty oils this matter of the influence of temperature has been investigated carefully by Maxted⁵ and the following is quoted from his article on "The manufacture of pure hydrogen and the catalytic hydrogenation of oils."

403. In many of the earlier plants, particularly those in which nickel oxide was used in place of nickel, a relatively high reaction temperature (200°–250° C.) was employed. It has, however, now long been recognized that relatively high temperatures influence adversely, both the quality of the product and the speed of reaction. The optimum working temperature will depend to a large degree on the nature of the nickel catalyst employed and on the oil to be treated, particularly in view of the fact that certain of the catalyst poisons appear to be less toxic at high temperatures, this factor tending to compensate for the decreased reaction velocity due to a temperature above the optimum point.

The following comparative figures, relating to the influence of temperature on the velocity, were obtained with refined olive oil under laboratory conditions. The volume of oil taken for each test was 10 cc., the catalyst consisting of 0.1 g. of nickel, reduced at 300° C.

Time in Mins.	Cc. of Hydrogen Absorbed at								
	80°	100°	120°	140°	160°	180°	200°	225°	250°
1	0.9	7.4	17.5	28.0	32.0	31.8	28.8	18.0	7.7
2	1.9	14.8	35.0	54.5	63.0	60.3	53.5	32.5	13.8
3	2.8	22.5	53.0	79.5	91.5	84.3	73.5	43.0	19.0
4	3.7	30.0	70.0	104.0	116.5	104.5	90.0	51.3	24.0
5	4.7	37.9	87.0	128.0	140.5	120.8	103.0	58.5	28.5
10	10.4	78.8	167.0	228.0	238.0	182.0	152.5	88.1	45.8
15	17.1	119.6	237.5	305.0	309.0	224.5	187.0	111.5	59.0
20	25.6	159.0	301.0	368.0	369.0	260.0	219.5	133.7	68.0
25	35.0	195.2	350.0	419.5	414.5	292.0	246.0	152.7	75.7
30	44.5	228.6	395.5	465.0	455.0	323.5	271.0	168.0	80.0

404. On plotting these figures graphically against the time, it is found that each of the graphs, with the important exception of those at comparatively low temperatures, such as 80° and 100°, is curved in form. At relatively low temperatures, with pure substances, the activity of the catalyst usually increases somewhat after this has been used for a short time, probably owing to the catalytic reduction of the nickel oxide usually contained in nickel catalysts. This phenomenon is exemplified by the course of the reaction at 80° in the above table.

405. With reactions of this nature, assuming that the activity of a catalyst is to be measured by the effect produced by it, the simplest method for obtaining comparative figures for the relative activity of the nickel under given conditions is to assume this to be proportional to the initial velocity of absorption of hydrogen, a value which is easily obtained by differentiation from the equation to the reaction curve. The following table contains the results of the preceding table treated in this way.

³ Studies in the hydrogenation of benzene, *J. Phys. Chem.*, 1923, **27**, p. 548.

⁴ With large quantities of CO (50 per cent) the reaction was stopped even at 180° C.

⁵ *J.S.C.I.*, 1921, **40**, 169T.

Temperature, Degrees C.	Relative Activity of Catalyst
80	1.0
100	7.8
120	17.5
140	28.5
160	34.0
180	35.0
200	32.0
225	21.0
250	8.5

406. If the above results are plotted graphically, it will be found that the temperature of maximum activity appears to be about 175° C. The velocity of reaction is appreciable even at 80°, while at 100° it is sufficient for this temperature to be used for efficient hardening. This result is opposed to many of the earlier publications; for instance, Ipatiev (*Chem. Zeit.*, 1914, 39, 374) stated that reaction between hydrogen and oil in the presence of nickel only begins at 150° C. The linear form of the reaction curves at low temperatures is well seen if the figures of table, para. 403, for 100°, 160°, and 200° C., are plotted. It has been shown elsewhere (*Chem. Soc. Trans.*, 1920, 117, 1501; 1921, 119, 225) that the addition of fixed amounts—i.e., of amounts which do not increase during the progress of hardening—of many catalyst poisons has little effect on the curvature of the absorption graph, although the speed of reaction is of course decreased thereby, and it would thus appear highly probable, from the difference in curvature obtained with nickel at low and high temperatures respectively, that catalyst poisons which cause curvature and a corresponding decrease in the activity of the catalyst are produced during the hardening operation itself when carried out at relatively high temperatures. The employment of temperatures in the region of 100° C. is only possible with relatively pure oils.

Maxted further states that with most oils, of average commercial quality, a somewhat higher reaction temperature is rendered necessary by the catalyst poisons in the oil itself, and it is his ordinary plant practice to begin hardening at about 120°–130° C., the temperature rising subsequently, by virtue of the heat of reaction, to a maximum of about 160° C.

407. Hitherto we have dealt with temperature variation as affecting only the reaction rate and the resistance to temporary poisons. Such are, indeed, the only sensible effects in most hydrogenations, within the hydrogenation range of temperature. There are, however, temperature effects of another order. The first is the change in the equilibrium of a reversible hydrogenation \rightleftharpoons dehydrogenation reaction, which at certain temperatures tends towards hydrogenation, while at others dehydrogenation predominates. The second class of temperature effect mentioned is a directive effect—sometimes this is merely another aspect of dehydrogenation.

408. Hydrocarbons of the benzene series and terpenes when passed with hydrogen over nickel at 180° C. are hydrogenated, but if the temperature is raised to 350°–360° C. dehydrogenation occurs. Thus, at the higher temperature, pinene, limonene, and camphene yield a mixture of cymene with some cumene; menthene gives cymene; cyclohexene at 300° C. gives benzene. The reaction may also be applied to oxygenated derivatives of the hydrocarbons. Cyclohexanol yields phenol; pulegone gives a mixture of cresol and thymol; eucalyptol, terpin and terpineol undergo dehydration as well as dehydrogenation. The mixture obtained by the destructive distillation of oil of turpentine, which is poor in benzenoid hydrocarbons, when passed with hydrogen over nickel at 350°–360° C., gives a liquid in which the proportion of benzenoid hydrocarbons is notably increased.*

* Sabatier and Gaudion, *Compt. rend.*, 1919, 168, 670; *J.S.C.I.*, 1919, 338A.

409. Of the directive effect of temperature instances may be culled from the section on hydrogenation of organic compounds. It will be seen that this temperature effect is often either a breaking up of the products of hydrogenation, or a partial dehydrogenation, controlled by the presence of a hydrogen atmosphere.

410. Phorone, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{C}(\text{CH}_3)_2$, hydrogenated over nickel at $160^\circ\text{--}170^\circ\text{C}$. is completely converted to di-isobutyl ketone (iso-valerone).⁷ Reduced at 225°C . for five hours in a current of hydrogen there is a 65 per cent yield of the ketone; at 235°C . there appear an unsaturated hydrocarbon, di-isobutylcarbinol and beta-zeta-dimethylheptane.⁸

Styrene, $\text{C}_6\text{H}_5\text{CH}:\text{CH}_2$, at 300°C ., over nickel, yields ethyl benzene, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$; at 180° ethylcyclohexane is produced.⁹

411. Hydrogenation at room temperature with nickel catalyst. Kelber¹⁰ has prepared a nickel catalyst capable of acting in hydrogenations at room temperature, e.g., in reduction of cinnamic acid. He precipitates nickel hydroxide on an inert support and reduces at a low temperature. Tomaka¹¹ confirms and extends these observations but states that the operation is slow and that the method demands a high degree of purity in the reactants. Rarely is a highly active catalyst also robust.

412. The relation between the temperature and the activity of nickel in catalyzing the reduction by hydrogen of ethylene to ethane, benzene to cyclohexane, and oxygen to water has been studied by following the pressure within a closed vessel containing the reactants and the catalyst when the temperature is gradually raised. It is found that with rising temperature there is a series of small temperature intervals in which there are sudden rapid increases in the reaction velocity, one of which is much the greatest and can be regarded as the transition from slow catalysis to rapid catalysis. The temperatures at which these effects commence are approximately the same, independent of the nature of the reaction and of the way in which the catalyst is prepared. In some cases, the reaction velocity passes through a series of minima. If the same catalyst is used for a consecutive series of reduction of ethylene or benzene not separated by any intervals, the temperature at which rapid catalysis commences gradually falls. Keeping the catalyst in an atmosphere of hydrogen or using it for the water synthesis has the reverse effect. No complete explanation of the observed phenomena can be advanced, but it is suggested that the temperatures at which sudden increases in reaction velocity occur may correspond with some kind of transitions in the catalyst.¹²

413. Selectivity by Phase. Lush¹³ found that in the hydrogenation of naphthalene with a nickel catalyst, in the vapor phase only tetralin could be

⁷ Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909 (8), 16, 73.

⁸ Skita, *et al.*, *Ber.*, 1908, 41, 2938; *J. Chem. Soc.*, 1908, 94, 855A.

⁹ Sabatier (tr. Reid), *Catalysis in Org. Chem.*, 362.

¹⁰ *Ber.*, 1916, 49, 55.

¹¹ *Chem. Ztg.*, 1924, 48, 25.

¹² Thoren, *Z. anorg. Chem.*, 1927, 163, 367; *Brit. Chem. Abst.*, 1927, 839A.

¹³ *J.S.C.I.*, 1927, 454T.

formed, whereas in the liquid phase decalin was produced. The total hydrogen absorbed was independent of the relative proportion of tetralin and decalin made. See paragraphs 4113 and 4120.

PRESSURE

414. Influence of the Hydrogen Pressure. The majority of hydrogenations will proceed at atmospheric pressure, though, even in such cases, there is sometimes a convenience in working at plus pressures. There are reactions whose direction may be controlled by increasing the pressure. This is typically the case where unsaturated side-chains are attached to nuclei, also susceptible of, but more resistant to hydrogenation. There are, again, hydrogenations for which no catalysts capable of acting at low pressures have been found: typical examples of these will be found among the carbon monoxide syntheses that have sprung into industrial prominence.

415. In the hydrogenation of phenol in the liquid phase at 150° C. with a nickel catalyst, the formation of cyclohexanol is very slow at atmospheric pressure, but is rapid and complete under 15 atmospheres of hydrogen pressure, at the same temperature.¹⁴

416. The studies of Armstrong and Hilditch¹⁵ on the influence of variation in the hydrogen pressure on hydrogenation at solid catalytic surfaces were conducted with great care and are more systematic than most of the other work reported. The outcome is that the velocity of hydrogenation is directly proportional to the hydrogen pressure, in the absence of disturbing factors. Among disturbing factors that have been recognized some are obvious (when once pointed out!) others are latent. Obvious influences are: the presence of slowly acting permanent catalyst poisons and the accumulation of gaseous impurities (acting as diluents) in the gas space. Less obvious is the preferential adsorption of gaseous impurities at the catalyst surface. Latent, that is hardly predictable, is, for example, the effect produced when the unsaturated compound contains a group not susceptible of hydrogenation but having an affinity for nickel. This effect consists in an augmentation of the influence of increase in the hydrogen pressure. In the presence of such a group the hydrogenation rate for a given pressure is accelerated. Among compounds exhibiting this phenomenon may be cited unsaturated alcohols and unsaturated carboxylic acids.

417. The unregarded existence and development during the operation of the disturbing factors which lead to a retardation of hydrogenation is suggested in explanation of the numerous instances in which earlier workers have found, not linear hydrogen-time curves, but curves suggestive of unimolecular reactions.¹⁶

418. In the article already quoted¹⁷ Maxted reports experiments made to

¹⁴ Brochet, *Bull. Soc. Chim.*, 1914 (4), **15**, 588; cf. *idem*, *Compt. rend.*, 1914, **158**, 1352, a discussion of the effect of temperature and pressure on hydrogenation.

¹⁵ *Proc. Roy. Soc.*, 1921, **100A**, 240.

¹⁶ Fokin, *Zeitsch. angew. Chem.*, 1908, **22**, 1451, 1492; Moore (H. K.), Richter and van Ardsdel, *Ind. Eng. Chem.*, 1917, **9**, 451; Ueno, *J. Chem. Ind. (Tokyo)*, 1918, **21**, 749; Ubbelohde and Svanoe, *Zeitsch. angew. Chem.*, 1919, **32**, 257, 269, 276; *J.S.C.I.*, 1920, **39**, 120.

¹⁷ Para. 402.

determine the influence of variations in the hydrogen pressure on the velocity of hydrogenation of fatty oils.

419. The apparatus consisted of the usual shaker, in which, however, the measuring burettes were replaced by a closed manometer. The whole apparatus was filled with hydrogen at an increased pressure, and, on shaking in the usual way, the absorption could be followed by the drop in pressure indicated by the manometer. For the sake of simplicity, the reaction was carried out at 100° C., the course under these conditions, with the catalyst and oil employed being, as already stated, linear when allowed to proceed without a variation in pressure.

420. If v represents the volume in cubic centimeters of hydrogen absorbed after t minutes, and if the rate of absorption is, for the moment, assumed to vary as the n th power of the pressure.

$$\frac{1}{P^n} \cdot \frac{dv}{dt} = k$$

where k is a constant.

421. From the manometer readings at various intervals of time it is, as already stated, easily possible to calculate the progress of absorption with the time, and, by differentiating the equations connecting these two quantities, the relative values of dv/dt corresponding to the various pressures are readily obtained.

422. The table below summarizes the results of a typical experiment with a varying pressure in a closed system of this sort. The striking constancy of the constant k , which has been calculated for $n = 1$ in the above equation, would appear to demonstrate beyond doubt that the rate of absorption of hydrogen at a constant temperature varies directly as the pressure:

Time in Minutes	Cc. Hydrogen Absorbed	Pressure in Atmospheres	$\frac{dv}{dt}$	k ($n = 1$)
0	0	2.06	15.66	7.60
1	15.0	1.915	14.61	7.64
2	29.5	1.785	13.60	7.62
3	42.5	1.65	12.63	7.63
4	54.5	1.53	11.70	7.64
5	65.0	1.42	10.82	7.63
6	75.5	1.32	10.03	7.61
7	85.0	1.23	9.17	7.47
8	94.5	1.14	8.40	7.36
9	103.5	1.05	7.72	7.35
10	111.5	0.97	7.00	7.22

423. **Catalytic Hydrogenation at Reduced Pressures.** Grignard¹⁸ has studied the catalytic hydrogenation of organic substances at low pressures, using nickel, copper, platinum-black, and platinum oxide as catalysts, with pumice as a supporting material. It is possible, by adjusting the pressure and temperature, to stop catalytic hydrogenations at the first stage, and to eliminate all secondary changes. In this way ethylenic alcohols such as the methylheptenols are quantitatively converted into the corresponding saturated hydrocarbons. Phenol is reduced to cyclohexenol, acid chlorides to the corresponding aldehydes, and benzaldehyde to benzyl alcohol. The reduction of nitriles can be stopped at the aldimine stage. Benzonitrile gave benzaldimine. Phenylacetoneitrile is completely reduced at 200°/220 mm. to phenylacetaldimine. Under

¹⁸ *Bull. Soc. Chim. Belg.*, 1928, 37, 41.

certain conditions, phenylacetonitrile is partly hydrogenated to a crystalline solid of m.p. 128–130°. ¹⁹

STIRRING

424. Catalyst Concentration, Stirring and Reactant Concentration. The influence of these factors on the reaction rate was studied by Lietz ²⁰ in the hydrogenation of sodium cinnamate over nickel. It was found that the velocity was proportional to the concentration of the catalyst and to the rate of stirring. It was independent of the concentration of sodium cinnamate. Lietz concludes that the reaction velocity is determined by the rate of diffusion of the hydrogen.

425. Effect of High-speed Stirring. This has been studied for the hydrogenation of cottonseed oil over nickel by Milligan and Reid. ²¹ Their conclusion is that the reaction rate is nearly proportional to the speed of stirring. The speed of stirring they used was about 13,000 r.p.m. The time of experiment was very short, so that the amount of absorption obtained by simply bubbling the gas through the mixture, without stirring, was negligible.

¹⁹ *Brit. Chem. Abst.*, 1928, 521A. See also Grignard and Mingasson; Escourrou.

²⁰ *J. prakt. Chem.*, 1924 (2), 108, 52.

²¹ *Ind. Eng. Chem.*, 1923, 15, 1048.

CHAPTER V

POISONS AND INHIBITORS

CATALYST POISONS

500. When dealing with negative catalysis we adverted to the subject of the poisoning of catalysts. A catalyst poison is a substance which inhibits, partially or completely, the activity of a catalyst.

This effect attracted the attention of the earliest workers on catalytic chemistry. Faraday, studying the combination of hydrogen and oxygen in presence of his platinum plates, noted that the addition of certain foreign gases caused a slowing up of the action. Nor was this retardation due merely to dilution, as was shown by the fact that the effect was not quantitatively the same for all gases. Carbon monoxide was one of the most important catalyst poisons discovered by Faraday.

501. In the chronology of early discoveries in catalysis, we recorded the fact that in 1831 a Bristol manufacturer named Phillips took out a British patent for the production of sulphur trioxide by the air oxidation of sulphur dioxide over platinum. This method of making sulphuric acid, now of great commercial importance, did not become an industrial success until ways were discovered of removing arsenical and other catalyst poisons from the pyrites-burner gases.

502. Not a few investigators, and among them the most eminent, have treated catalyst poisoning as a special case of negative catalysis. Some have, admittedly, done this for reasons of convenience: others evidently regard this classification as correct.

It is difficult to understand the views of these last. If we are to assemble catalyst poisons into one class, we cannot well make it a subdivision of negative catalysts. Opinions differ as to what are the criteria of a catalyst: but there is an irreducible minimum upon which all agree. No one disputes that (side reactions apart) a catalyst is chemically unchanged at the end of the reaction. Now a large number of catalyst poisons react with the catalyst to form compounds which are of the "permanent" class. Such poisons would be aliens in any group of catalysts, positive or negative.

503. The small quantities of some catalyst poisons which suffice to produce inhibitory effects have influenced various writers to assimilate them all to negative catalysts. But a little reflection will show that the analogy is fallacious. A poison may be small in proportion to the reactants whose interaction it inhibits, and yet not so small in comparison with the material on which it really acts

viz., the active area of the catalyst surface. Nor should it be forgotten that the poison produces its effect by a single intervention at the catalyst. This is in strong contrast with the characteristically repetitive action of a true catalyst.

504. The bullet of Serajevo was infinitesimal in comparison with the catalysm it let loose on the world: but its mass was large in comparison with that of the vital structures that it severed in its single passage.

505. Poisons may be either permanent or transitory. When a permanent poison has impaired the activity of a catalyst, the latter must be regenerated or replaced. In the case of a temporary poison the continuance of the process may lead to its elimination.

506. Hydrogen sulphide is a permanent poison to the nickel catalyst used in so many important hydrogenations. It combines with the metal with the formation of the inert sulphide, which is stable under the conditions.

507. Silicon compounds, present in the ammonia-air mixture, permanently poison the platinum gauze used to catalyze the oxidation of ammonia. In this instance the effect is grossly mechanical, being due to the deposit of a layer of silica which shuts off the platinum surface from contact with the reactant gases.

508. Water is a transitory poison to the iron catalyst in ammonia synthesis.

509. The problems of catalyst poisoning are of great practical importance, both in the laboratory and in the factory, and, especially, in the stage of transition between a satisfactory laboratory solution of a problem and its industrial application in the factory.

510. In the laboratory one of the occasional difficulties is due to the extreme sensitiveness of some catalysts which causes them to be completely inhibited by mere traces of an obscure impurity.

511. Berliner showed that traces of fatty vapors from the air or from the grease on the stopcocks decreased the adsorption of hydrogen by palladium from nine hundred volumes to zero. Pollard observed a like diminution in the adsorption by platinized asbestos from about one hundred and forty volumes to a negligible amount.¹ It has been shown in the section on the theory of catalysis that there is an intimate relation between adsorption and catalytic activity.

512. Even more remarkable is the action of minute traces of poisons in abolishing, not all the activity of a catalyst, but only its power to catalyze a special reaction. Such an effect may be called a directive poisoning. It is a poisoning of the reactants, perhaps of the reaction, rather than of the catalyst.

513. Sabatier found that benzene containing scarcely detectable traces of thiophene could not be catalytically hydrogenated to cyclohexane. Kubota and Yoshikawa² were able to confirm this inhibitory action of thiophene,³ but the nickel catalyst, so poisoned, was still active for the hydrogenation of phorone.

514. Nickel used to hydrogenate phenol for only a day or two will still hydrogenate cresol, but after a month's use on phenol, it is inactive on cresol, though still active on phenol. The activity for cresol can be regenerated by oxidizing the catalyst and then reducing it.

¹ First Report of the Committee on Contact Catalysis, 1922, p. 19.

² *Sci. Papers Inst. Phys. Chem. Res. (Japan)*, 1925, **3**, 33.

³ *Cf. Ardagh and Furber, Removal of thiophene from benzene, J.S.C.I.*, 1929, **48**, 73T.

515. Although the action of poisons is one of the best understood parts of the catalysis problem, nevertheless the selective action of poisons is in some instances unpredictable to the verge of sheer capriciousness. Thus Sabatier and Espil were able to hydrogenate benzene containing 10 per cent of carbon disulphide, though a mere trace of thiophene instantly stopped the reaction.⁴

516. The sensitiveness to poisoning of some otherwise suitable catalysts renders them unutilizable on the large scale.

517. In the ammonia synthesis, using uranium carbide (which changes to nitride) as catalyst, water vapor, oxygen and monoxide are permanent poisons. The nitride is converted to an irreducible uranium oxide, catalytically inert. This precludes the use of an otherwise excellent catalyst in ammonia synthesis.

518. Concerning the phenomena of catalytic poisons, Bancroft⁵ remarks that the adsorption of reacting substances and consequently reaction velocity are decreased by the presence on the solid catalytic agent, of a film of solid, liquid, or gas. Very small amounts of grease will keep palladium from taking up hydrogen. Carbon monoxide may act as a catalytic poison by decreasing the adsorption of other substances. It is very tenaciously held by platinum. Reaction products may decrease reaction velocity by hindering diffusion of reacting substances to the catalytic agent and by decreasing their adsorption.

519. Pease and Stewart⁶ have made quantitative measurements of the influence of carbon monoxide on the activity of a copper catalyst towards a mixture of ethylene and hydrogen at 0°. They find that the catalyst is very sensitive to the poison, less than 0.05 cc. of carbon monoxide being sufficient to reduce the catalytic efficiency of 100 g. of copper by 90 per cent. It appears that the metallic surface owes 90 per cent of its efficiency as a catalyst to less than 1 per cent of the regions which are active in adsorption. Adsorption measurements, even at pressures as low as 1 mm., furnish no trustworthy index of catalytic activity for hydrogenation catalysts. Carbon monoxide is a "temporary" poison, pumping out at 250° being sufficient to restore the activity of the catalyst.⁷

520. Kelber has found that nickel catalysts made in different ways behave entirely differently, in reducing reactions, toward contact poisons such as hydrocyanic acid or potassium cyanide, hydrogen sulphide and carbon bisulphide.⁸

521. The following catalysts (a) from basic nickel carbonate reduced at 450° in hydrogen (b) from basic nickel carbonate reduced in hydrogen at 310° and (c) from basic nickel carbonate on inorganic carriers reduced in hydrogen at 450°, show a sensitiveness to these poisons, decreasing in the order (a), (b) and (c). This is believed to be due to the fact that the high temperature at which (a) is prepared changes the surface of the individual particles of the catalyst so that there remain only a few points on these particles which are capable of adding hydrogen and acting as a carrier of it, and these points, being more reactive than the rest of the nickel are the first to act on the poison, so that relatively small amounts of the latter are able to poison the whole of the catalyst. The lower temperature used in preparing (b)

⁴ Sabatier (tr. Reid), *loc. cit.*, 114.

⁵ *J. Phys. Chem.*, 1917, **21**, 734; *Chem. Abst.*, 1918, **12**, 328.

⁶ *J. Amer. Chem. Soc.*, 1925, **47**, 1235.

⁷ Cf. Constable. Effect of continued small additions of poisonous substances on the velocity of gaseous catalytic reactions in closed vessels. *Proc. Camb. Phil. Soc.*, 1927, **23**, 832. Theoretical discussion on and corollaries to Pease and Stewart, *loc. cit.*

⁸ *Ber.*, 1916, **49**, 1868.

leaves more of these active spots, while in (c) the presence of the inorganic skeleton doubtless hinders the change in the surface of the catalyst. The experiments were carried out at room temperature under atmospheric pressure in a shaking apparatus, 0.5 g. of the metal being shaken twenty minutes with the poison in 25 cc. water in a hydrogen atmosphere, then treated with sodium cinnamate (0.75 g. acid and somewhat more than the calculated amount of caustic soda in 25 cc. water) and the absorption of hydrogen measured every five minutes.

522. Below are given the per cent of its original value to which the reducing power of the 3 catalysts is decreased by varying amounts of the different substances in the first fifteen minutes. Potassium cyanide: (a) 0.00005 g., 45 per cent; 0.0003 g., 2 per cent; (b) 0.0003 g., 55 per cent; 0.001 g., 0 per cent; (c) 0.002 g., 25 per cent; 0.02 g., 2 per cent. (It is not clear in the original whether the amounts given above represent the weights of potassium cyanide used or the amounts of hydrocyanic acid equivalent to the salt used.) Hydrocyanic acid: (a) 0.0005 g., 63 per cent; 0.002 g., 1 per cent; (b) 0.001 g., 50 per cent; 0.005 g., 0 per cent. Traces of alkalis give entirely different values and as (c) could not be entirely freed of alkalis it was not used in this series. The small "toxicity" of hydrocyanic acid as compared with potassium cyanide is ascribed to the rapid change of hydrocyanic acid in the presence of nickel and hydrogen; the catalysts poisoned with hydrocyanic acid retain only traces of the poison, whereas with potassium cyanide, the catalyzer shows large amounts of the poison, although in a changed form. To test the effect of hydrocyanic acid, potassium cyanide and nickel cyanide on the catalyst, (b), after saturation with hydrogen was shaken in hydrogen to constancy of volume with definite amounts of solutions of the 3 substances, filtered, and the poison determined in the solid and the filtrate; the filtrate was found to be free from hydrocyanic acid but to be strongly alkaline and contain ammonia, probably produced by a catalytic reduction of hydrocyanic acid or a nickel cyanide compound, as several cubic centimeters of hydrogen were always used up; the solid nickel, when dissolved in sulphuric acid and heated with alkali, gave a distillate containing ammonia; no amines, or only traces at most, were found in the solid or filtrate. A catalyst poisoned with potassium cyanide, then filtered and washed with water, does not recover its activity, but this can be restored by treating once with hydrogen and warming with ammonia, or, best, by boiling with caustic soda.

Hydrogen sulphide: (a) 0.001 g., 25 per cent; 0.005 g., 1 per cent; (b) 0.01 g., 15 per cent; 0.02 g., 0 per cent; (c) 0.02 g., 60 per cent; 0.1 g., 0 per cent. The sulphur is found almost entirely as sulphide, in the solid nickel.

Carbon bisulphide: (a) 0.0005 g., 25 per cent; 0.003 g., 0 per cent; (b) 0.003 g., 60 per cent; 0.01 g., 1 per cent; (c) 0.01 g., 63 per cent; 0.06 g., 3 per cent. Practically all of the sulphur found (corresponding to about 50 per cent of that in the carbon bisulphide used) was in the solid nickel as sulphide, with only traces in the filtrate.

523. Sulphur, Arsenic, Halogens, etc., as Catalyst Poisons. Sabatier and Espil have concluded that the effect of sulphur and the halogens as catalyst poisons has been exaggerated. Traces of these substances do not appear sufficient to destroy the activity of nickel. For example benzene containing 0.5 per cent iodine in solution was completely transformed into cyclohexane. The nickel in about one-half of the hydrogenating tube toward the inlet side was affected but the catalyzer in the other half of the tube remained active. Chlorine and bromine, introduced as hydrochloric or hydrobromic acids or as halogenated benzol, also sulphur in the form of carbon bisulphide, acted in a similar manner. Moreover, the nickel which is rendered inactive to benzol still preserves the power of carrying hydrogen to nitriles and other aliphatic or aromatic organic compounds but is incapable of hydrogenating ketones or ethylene hydrocarbons. Sabatier and Espil recommend that nickel poisoned by chlorine be revived by using it to hydrogenate nitrobenzene. After a few hours' use in this manner the catalyzer is reactivated and will convert benzene into cyclohexane. When poisoned by bromine or iodine this treatment is not effective.⁹

524. It has generally been assumed that presence of sulphates in a nickel catalyzer is prejudicial but repeated tests by Ellis have shown this not to be the case under certain conditions. If the sulphate is of a difficultly reducible character as, for example, sodium sulphate, the nickel is practically unaffected, especially if the reduction has taken place at a relatively low temperature. When a

⁹ *Bull. Soc. Chim.*, 1914, 15, 778.

mixture of nickel hydrate or carbonate and sodium sulphate is reduced at a temperature somewhat below 250° C. the activity of the catalytic nickel is not materially affected by the sulphate. Apparently, sulphur in the sulphide form is necessary in order to poison the catalyzer. Catalytic material containing sulphates has been employed on a commercial scale in this country for a considerable period of time with satisfactory results.

525. The effect of sulphur and arsenic in hydrogen gas employed for oil hardening has been investigated by Hehner and reported by Crossley.¹⁰ Curves of absorption were obtained which indicate the deleterious action of arsenic and sulphur. Unpurified hydrogen such as was obtained from a good specimen of zinc and acid did not permit the catalyzer to function as actively as in the case of pure hydrogen. When hydrogen was passed through a very dilute solution of hydrogen sulphide in water the effect on the catalyzer was very marked. The effect of using crude water gas containing about 28 per cent of hydrogen in comparison with water gas which has passed through soda lime is shown by Hehner. The purified water gas permitted catalytic action to go on to better advantage.

526. Poisoning of Nickel Catalysts by Iron and Nickel Compounds. Wolff¹¹ reports that in the catalytic hydrogenation of cinnamic acid in alkaline aqueous solution by nickel, the addition of ferric or nickel hydroxide brings about at first a sharp fall in activity, proportional to the amount of "clogging substance" added, later a slower decrease, but again proportional to the amount added. It seems that the more active parts of the catalyst are more sensitive to the foreign substance. Similar behavior is shown if a soluble substance be present, potassium ferrocyanide, for example. Here it is suggested that the ferrocyanide ion is adsorbed and that the break in the activity-concentration curve occurs when the film covers the whole surface of the catalyst.¹²

527. Fatigue of Platinum Black. Vavon and Husson¹³ observed gradual fatigue of platinum black in catalyzing hydrogenations.

528. Consider three substances, A, B and C, capable of hydrogenation. The rate of fatigue may be different so that B and C are catalyzed while A is not, and later only C is catalyzed. The fatigue may be caused by (a) too long employment in catalytic operations, (b) heating to too high a temperature, (c) partial poisoning by a suitable substance. It is the last which is the subject of this investigation.¹³ The mode of operation consists in agitating the substance to be hydrogenated, in solution, in the presence of the platinum and in an atmosphere of hydrogen. If in the course of the experiment successive additions are made of carbon disulphide, an abrupt diminution of the velocity of hydrogenation takes place after each addition until complete cessation of the reaction. This limit varies with the nature of the substance, and is proportional to the weight of platinum employed. An explanation of this phenomenon on the basis of the formation of a reactive hydride of platinum is not satisfactory, since there would have to be any number of different hydrides. The following explanation is offered: The surface of the catalyst adsorbs the hydrogen mole-

¹⁰ *Pharm. Soc.*, April 21, 1914; *Pharm. J.*, 1914, **92**, 604, 637 and 676; *J.S.C.I.*, **1914**, 1135.

¹¹ *J. prakt. Chem.*, 1924, **107**, 159-164.

¹² *J.S.C.I.*, 1924, 574B.

¹³ *Compt. rend.*, 1922, **175**, 277; *Chem. Abst.*, 1922, **16**, 3792.

cule making it subject to a deformation, the deformed molecule becoming active. This deformation is a function not only of the nature of, and radius of curvature of the catalyzer surface, but also of the substance already adsorbed by this surface (oxygen, solvent, carbon disulphide, etc.). Some substances favor deformation (e.g., oxygen), others the contrary (carbon disulphide). The greater the amount of carbon disulphide, the less the deformation. It is further necessary to assume that there is a minimum deformation required for each reactive substance.

529. Rocasalano¹⁴ has observed this phenomenon. He reports that the catalytic activity of electrosols of platinum and hydrosols of palladium in regard to the decomposition of hydrogen peroxide increases at first with age until it reaches maximum and then decreases.

530. Influence of the Support on the Resistance to Poisons. Rosenmund and Langer¹⁵ carried out a series of experiments on the rate of catalytic reduction of cinnamic acid by hydrogen with the aid of a palladium catalyst deposited upon various supports and in presence or absence of two "poisons" (arsenious oxide and carbon monoxide). Kieselguhr-palladium catalysts showed the least activity and the greatest sensitiveness to poisoning, while palladinized blood charcoal was both the most active and the most resistant catalyst. In both these cases the activity of the catalyst runs parallel to its resistance to poisoning, but this is not invariably the case. The general conclusion drawn from the experiments is that the influence of a third substance on a catalyst varies according to the nature of the support on which the catalyst rests. The following figures indicate the results obtained using as carriers (a) crude kieselguhr; (b) purified kieselguhr; (c) purified pumice powder; (d) barium sulphate; (e) purified bone charcoal; (f) purified blood-charcoal. (The figures indicate the average rate of hydrogen absorption in cubic centimeters per minute): I. Normal experiments: (b) 0.70; (e) 1.25; (a) 1.90; (c) 2.05; (d) 2.30; (f) 6.20. II. As₂O₃ poisoning: (b) 0.00; (a) 0.00; (d) 0.23; (c) 0.40; (e) 0.43; (f) 4.25. III. CO poisoning: (b) 0.25; (d) 0.45; (a) 0.80; (e) 1.00; (c) 1.65; (f) 5.45.

531. Intentional Partial Catalyst Poisoning Used to Limit Reaction. We have already learned (para. 513) that the presence of traces of thiophene inhibits the catalytic hydrogenation of benzene in the presence of nickel, but leaves intact the catalytic activity for other substrates. Kubota and Yoshikawa¹⁶ have availed themselves of this peculiarity to limit the hydrogenation of nitrobenzene to the formation of aniline. It is the opinion of these workers that catalytically active nickel consists of various hydrides. Poisoning by thiophene, by ethyl sulphide, and by hydrogen sulphide inhibit, respectively, the hydrogenation of the aromatic nucleus, the hydrogenation of unsaturated aliphatic compounds, and the reduction of nitrobenzene to aniline. These three stages in poisoning correspond with formation of definite quantities of nickel sulphide. Advantage may be taken of these facts for the production of aniline. Nitrobenzene is intro-

¹⁴ *Compt. rend.*, 1920, 171, 301.

¹⁵ *Ber.*, 1923, 56, 2262-2264.

¹⁶ *Sci. Papers Inst. Phys. Chem. Res.*, 1923, 3, 223-232.

duced into a reaction tube with hydrogen and thiophene-poisoned nickel at 180°. The condensed liquid consists of two colorless layers. The lower layer is separated from the water and dried; it can be distilled completely at the boiling-point of aniline. With the unpoisoned catalyst the reaction product contains only 38 per cent of aniline.)¹⁷

532. Rosenmund and Zetsche also have made use of partial poisoning in order to increase the yield of a desired product. If an acid chloride, benzoyl chloride for instance, is dissolved in pure benzene and is then subjected to reduction by means of hydrogen and colloidal palladium, practically no benzaldehyde is formed. It seems that the benzene is responsible for exerting a deterrent action on the palladium. If the experiment is tried with ordinary benzene, a good yield of benzaldehyde is obtained. This seemed to prove that some impurity in the benzene counteracted the poisoning. Instead of searching for the particular impurity in the benzene which had this action, the effect of adding known amounts of definite substances to the pure benzene or other aromatic hydrocarbon was examined. With 2 g. of benzoyl chloride in 10 cc. of xylene and using 0.7 g. palladium at 150°, addition of 1 mg. of thioquinanthrene brought the yield up to 78 per cent, while addition of sulphurized quinoline (impure thioquinanthrene) brought the yield up to nearly 90 per cent. Addition of 0.1 mg. distilled quinoline reduced the yield practically to zero because the reduction went further—to benzyl alcohol. Addition of xanthone accelerates the reaction between benzoyl chloride and benzyl alcohol forming benzyl benzoate. In toluene as solvent instead of xylene, benzyl benzoate is the chief product because the toluene checks the reaction between benzyl benzoate and hydrogen which gives rise to benzoic acid and toluene.¹⁸

533. Regeneration *in situ* of Sulphur-poisoned Metallic Catalysts. Prudhomme¹⁹ treats metallic and oxide catalysts, which have become inert through partial conversion to sulphides, with vapors of an organic acid such as acetic acid at, say 100° C. When sulphuretted hydrogen ceases to be evolved, the acid vapors are cut off and the temperature raised to that at which the salt is decomposed (say 150° C). The acid is, in part, recovered. This process requires no dismantling of the apparatus, the whole operation being conducted *in situ*. It is particularly applicable to plants for the manufacture of light synthetic hydrocarbons from carbonaceous materials of low value.

534. Purification of Hydrogen for Ethylene Synthesis. The Elektro-Chemische Werke G. m. b. H. find that the production of ethylene from acetylene and hydrogen on a commercial scale is difficult, due to the gradual loss in the efficiency of the catalyst. Even though the usual precautions are taken to remove the recognized poisons, such as hydrogen sulphide, sulphurous acid, chlorine and the like, there still remain in the gas certain impurities which cannot be eliminated by the usual absorption reagents. Accordingly it is recommended

¹⁷ *J.S.C.I.*, 1925, 953B.

¹⁸ *Ber.*, 1921, 54B, 435, 638, 1092; 1918, 51, 585; First Report of the Committee on Contact Catalysis, p. 26.

¹⁹ U. S. Pat. 1,640,668, Aug. 30, 1927.

to wash the hydrogen with concentrated sulphuric acid, then to pass it over solid caustic soda, which treatment is said to remove the troublesome bodies.²⁰

535. On the industrial scale it is rarely possible to use chemicals of the highest purity or to protect the catalyst from accidental contamination. The first care of the industrial catalytic chemist is to secure a catalyst of the maximum robustness, sacrificing, if needs must, some activity. Next he endeavors by scrubbing, to purify his gases, usually, in the cases which concern us, hydrogen or water-gas. Then he turns his attention to the raw material, which is likely to vary in its content of potential catalyst poison. Finally he arranges his operations so that the regeneration or replacement of catalyst shall cause only the minimum interruption. We will here mention one interesting instance of the preparation of a raw material to render it suitable for hydrogenation:

536. The hydrogenation of naphthalene for the production of fuels, solvents, etc., has become important in recent years. But commercial naphthalene contains sulphur compounds from which it should be purified before hydrogenation. In Schroeter's processes this is effected in various ways, e.g., by fusing the naphthalene with finely divided metal (iron or nickel), or a readily fusible metal or alloy (such as sodium), or metal loosely bound to nonacid radical, e.g., soda-mide. The purified naphthalene is recovered by distillation.

CATALYST POISONING IN OIL HARDENING

537. We have judged it advisable to treat separately the question of the poisoning of catalysts used in the hydrogenation of fatty oils because this industry has its special problems.

538. Effect of Various Acidic and Basic Substances on Nickel Catalysts. Kita, Masume and Kino²¹ reported that, in the hardening of soya-bean oil, sodium carbonate acted injuriously on the nickel-kaolin catalyst. It is now reported that both sodium carbonate and sodium borate at a concentration of 0.01 *N* have an accelerating effect, whereas at concentrations above about 0.1 *N* a retarding action is shown. Experiments were also made by bubbling the hydrogen through solutions of volatile substances (formic, acetic, propionic, butyric, and hydrochloric acids, ammonia, hydroxylamine, and aniline). In general, each of these volatile substances showed an accelerating influence on the hydrogenation of herring oil up to a certain concentration, and after that point a retarding effect as the concentration was increased. With a nickel-kieselguhr catalyst water vapor had a favorable effect on the hydrogenation of sesame oil, which was a maximum when the hydrogen was mixed with about 20-30 per cent by volume of water vapor. A similar favorable effect was also produced by mixing nitrogen with the hydrogen, the maximum being at about 48 per cent N_2 . With a technical basic nickel formate catalyst, on the other hand, addition of water vapor to the hydrogen had an unfavorable effect.²²

539. In connection with the use of palladium catalysts the Vereinigte chemische Werk. A.-G.²³ caution against the poisonous action of arsenic, phosphoretted and sulphuretted hydrogen, liquid hydrocarbons, carbon bisulphide, chloroform, acetone, and free mineral acids. Several of these poisons may find their way into the material during extraction or refining, while others are likely impurities in the hydrogen.

²⁰ *Zeitsch. f. angew. Chem.* 1913, Ref. 644; Ger. Pat. 265,171, 1912.

²¹ *Mem. Coll. Eng., Kyoto*, 3, [7]; *J.S.C.I.*, 1925, 964B, abstract of article by Normann, *Chem. Umschau*, 1925, 32, 262-265.

²² *J.S.C.I.*, 1925, 964B.

²³ Ger. Pat. 236,488, Aug. 6, 1910; Brit. Pat. 18,642, 1911.

540. The following table is taken from a paper by Ellis and Wells.²⁴

EFFECT OF HALOGENS, HALOGEN COMPOUNDS, SULPHUR, ETC., ON
HYDROGENATION OF COTTONSEED OIL

CATALYST: NICKEL OXIDE (5 PER CENT OF THE WEIGHT OF THE OIL) REDUCED
IN OIL AT 250° C. FOR ONE-HALF HOUR

Expt. No.	Substance Added	Per Cent Added	Temp., Degs. C.	Time, Hours	Effect on Oil
1	Bromine	1.0	200	2	No hardening
1 (CH)		1.0	200	2	
2	Iodine	1.0	200	2	
2 (CH)		1.0	200	2	
3		0.5	200	2½	Oil hardened
3 (CH)		0.5	200	2½	
4	Antimony bromide	1.0	200	2	
4 (CH)		1.0	200	2	
5	Sodium chloride	5.0	210	2½	Oil hardened
6	Zinc chloride	5.0	210	2½	
7		1.0	200	2½	
7 (CH)		1.0	200	2½	
8		0.5	200	2½	Slight hardening
9	Tin chloride	1.0	200	2	
10	Sulphur	0.5	200	2½	
10 (CH)		0.5	200	2½	
11		1.0	200	2½	No hardening
11 (CH)		1.0	200	2½	
Blank		200	2½	
12	Sulphur	0.1	210	3½	
13	Red phosphorus	1.0	200	2	Slight hardening
13 (CH)		1.0	200	2	
14		0.5	200	2	
14 (CH)		0.5	200	2	
15	Sulphur chloride	1.0	200	2	No hardening
15 (CH)		1.0	200	2	
16	(As ₂ O ₃)	1.0	200	2	
17	Mercury	1.0	200	2	
Blank		200	2½	Oil hardened
18	Lead stearate	1.0	200	2½	
19	Lead oleate	1.0	200	2½	
19 (CH)		1.0	200	2½	

(CH) after an experiment number indicates treatment with copper hydrate before hydrogenation.

541. The effect of catalyst poisons has also been studied by Moore, Richter and Van Arsdel.²⁵ The experiments on poisons were carried out in an apparatus containing oil and catalyst, through which hydrogen was bubbled. A mixture of oil with 1 per cent nickel on a carrier was hydrogenated first for one hour to ascertain the original activity of the catalyst. At the end of the hour, 2 per cent of the finely powdered solid substance in question was added, and the hydrogenation continued. Samples were then taken at intervals to determine the further fall of the iodine number, and the poisoning effect was judged by the shape

²⁴ *J. Ind. Eng. Chem.*, 1916, 886.

²⁵ *J. Ind. Eng. Chem.*, 1917, 451.

of the iodine number-time curve, compared with one in which no poison was present. The results may be summarized as follows:

Substance	Effect on Activity
Sulphur.....	Destroyed immediately
$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	Gradually destroyed
NaCl	No effect
Na_2SO_4	No effect
NaNO_3	No effect
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	No effect
Reduced iron.....	No effect

The three gases hydrogen sulphide, sulphur dioxide and chlorine were also tried. In each case the activity was destroyed immediately. A small amount of water vapor in the hydrogen was found gradually to destroy the activity of the catalyst.

542. The work of Maxted²⁶ indicates that carbon monoxide retards the rate of addition of hydrogen to fatty oils. The inhibitive effect of carbon monoxide was studied from a quantitative standpoint for the hydrogenation of olive oil, using finely divided nickel as catalyst. The experiments were carried out with 10 g. of oil and 0.1 g. of nickel, using pure hydrogen, and hydrogen containing 0.25, 0.5, 1.0 and 2 per cent of carbon monoxide respectively. The absorption was noted at five-minute intervals for one hour, at the end of which pure hydrogen showed 584.5 cc. absorption, hydrogen containing 0.25 per cent carbon monoxide, 393.9 cc.; hydrogen containing 0.5 per cent, 309.6 cc.; hydrogen containing 1.0 per cent, 235.2 cc.; and hydrogen containing 2 per cent, 158.8 cc. Maxted considers these results to show a marked poisoning influence by carbon monoxide, an effect which was differentiated from the calculated obstructive effects of the impurity. The first traces of carbon monoxide have relatively the greatest retarding influence on the velocity of hydrogenation.

543. Caro,²⁷ also, considers the presence of carbon monoxide in hydrogen used for hardening fats with nickel catalyzers to be, under some circumstances, injurious to the catalyzer. Maintaining the temperature of the oil during hydrogenation above 200° C. is said to be beneficial as any nickel carbonyl formed will be at once decomposed at that temperature. The hydrogenation of many substances under these conditions is not feasible and Caro recommends that the gas first be passed over nickel at 180° C. to convert the carbon monoxide into methane, which is inert.

544. Ueno²⁸ investigated the effect of a number of substances on the hydrogenation of oil with a nickel catalyst. The method he employed was to compare the fall of the iodine value when the oil was hydrogenated in the presence of the substance under investigation with the fall in a blank hydrogenation. He found that hydrogenation by means of a nickel catalyst was retarded by the soaps of potassium, sodium, lithium, magnesium, barium, beryllium, iron, chromium, zinc, cadmium, lead, mercury, bismuth, tin, uranium, and gold, while the soaps of calcium, strontium, aluminium, cerium, nickel, manganese, copper, silver, vanadium, thorium and platinum had no effect upon the catalytic action. Nickel acetate, butyrate, stearate, lactate, oxalate, and succinate had also no influence on the catalytic hydrogenation.

²⁶ *Trans. Faraday Soc.*, 1917; *Chem. Trade J.*, 61, 509-510.

²⁷ *Seifen. Ztg.*, 1913, 852.

²⁸ *J. Chem. Ind.*, Tokyo, 1918, 21, 898-939; *J.S.C.I.*, 1919, 20A.

Copper hydroxide, ammonium molybdate, boric acid, arsenious acid, hydrochloric acid, and potassium hydroxide had a strong restrictive effect, zinc oxide and aluminium silicate had a slighter effect, and tungstic acid was almost inert. Fatty acids, such as acetic, lauric, stearic, and oleic acids had no influence on the catalytic action, but glycollic and lactic acids, hydroxy-stearic acids, oxalic, succinic, and fumaric acids, and hydroxy acids, such as malic, citric, and tartaric acids, acted as catalyst poisons. Sodium taurocholate had a restrictive influence, while nucleic acid had no effect. Powdered metals (not reduced by hydrogen), such as nickel, tin, zirconium, aluminium, and copper had no pronounced injurious effect, but iron, zinc, lead, and mercury acted as poisons. Sulphur, selenium, tellurium, and red phosphorus acted as negative catalysts, but the presence of a small amount of oxygen in the hydrogen had no pronounced effect. Proteins, blood albumin, blood fibrine, and gelatine had a restrictive influence, but haemoglobin was inert. Glycerol and lecithin had a considerable action, but cholesterol and squalene had no effect. Carbohydrates such as sucrose, dextrose, mannitol, and starch behaved as negative catalysts, but glycogen had no influence. Alkaloids such as morphine and strychnine were pronounced poisons, as were also potassium cyanide, amygdalin, and the gaseous and liquid products of the dry distillation of herring oil.

545. Bedford and Erdmann²⁹ treated a quantity of used nickel oxide catalyst with dilute sulphuric acid. Hydrogen, accompanied by hydrocarbons of disagreeable odor, was evolved. A carbonaceous residue amounting to 6 or 7 per cent remained after treatment with the acid. Nickel oxide has been found to take up silica when used repeatedly as a catalyzer. The same absorption of silica also occurs with palladium.

546A. Sosenskii³⁰ gives the results of experience in the maintenance of nickel catalyst activity in the hydrogenation of oils. He finds that the part of the nickel which does not spontaneously settle out from the oil is inactive: it has been poisoned. But that part which settles out before filtration can be re-used by working up with make-up fresh catalyst.

546. Pretreatment of Oils to Remove Poisons. From an industrial point of view the protection of the catalyst from deterioration due to catalyst poison in crude oils subjected to hydrogenation is an important element in the economic working of hardening processes.

547. Ellis and Wells³¹ have studied the problem of treating such oils to adapt them to the hydrogenation process.

Usually the activity of the catalyzer becomes much slower after two or three batches of oil have been hardened and in some cases it is necessary to prepare fresh catalyzer for every batch of oil treated. On the other hand, when hardening a good grade of oil, such as refined, edible cottonseed oil, the life of a carefully prepared catalyzer is likely to be very long and in some cases an entirely new lot of catalyzer is not required for months in the constant operation of a hardening plant. In these cases the catalyzer is kept in a state of high activity for continued usage by adding a small amount of fresh catalyzer at intervals of one or two weeks. It has been observed that some kinds or grades of oil may be hydrogenated to an incomplete degree but that they cannot be carried beyond this point, no matter how long the treatment is continued, without change of catalyzer. If to these semi-hardened oils a fresh quantity of catalyzer is added the hardening will usually proceed practically to complete saturation. In some cases, a fresh quantity of oil may be treated with the seemingly spent catalyzer when partial hardening will occur. An additional quantity of fresh catalyzer will sometimes carry the oil so treated to completion, showing that the substance which affects the catalyzer is apparently taken up by it under these circumstances, thus leaving the oil in condition to be readily hardened.

²⁹ *Jour. prakt. Chem.*, **1913**, 444.

³⁰ *Oil and Fat Ind.* (Russia), **1926**, Nos. 4-5, 54-57; *Chem. Zentr.*, **1927**, I, 2868; *C. A.*, **1928**, **23**, 3308.

³¹ *J. Ind. Eng. Chem.*, **1916**, 886. See also U. S. Patent to Ellis, 1,247,516, Nov. 20, 1917.

548. A method of removing catalyst poisons from oil, recommended by Ellis, is to treat the oil with catalyst which has lost its catalytic activity. To this end a finely divided spent nickel catalyst is vigorously agitated with the oil at a temperature of about 180° C., until catalyst poisons have been absorbed when the oil is filtered, fresh catalyst added and hydrogenation is completed. The treatment of the oil depends upon the character of the catalyst poisons present. Aluminum, nickel, copper, etc., and their basic compounds in a finely divided state can be used.²²

549. This method, treating the oil with spent catalyst in order to remove catalyst poisons, is at present in extensive use. Its application is particularly economical in dealing with marine oils with which the life of the main catalyst is very short unless most of the poisons are removed.

550. Ellis and Wells²³ have reported an extensive series of tests bearing on this method of pretreatment.

551. Cod Oil. Crude cod oil was freed from fatty acids with a solution of sodium carbonate and after washing free from alkali and soap was treated with hydrogen, using 5 per cent catalyzer prepared from nickel oxide. In several trials, the oil either did not harden at all, or only to a very minor degree. Other forms of catalyzer were equally ineffective. The oil was then agitated for one hour at 200° C. with freshly prepared copper hydrate, filtered to remove the copper compound and again treated with hydrogen and catalyzer under the same conditions as above. The oil was readily hardened by this treatment. Another sample of the oil, refined as above, was treated with 5 per cent freshly prepared silver oxide at 200° C. for one hour. The silver compound was removed by filtration and the clear oil hydrogenated. In a short time this oil was hardened to a melting-point of 46° C. on hydrogenating under the same conditions as above.

552. A series of tests were performed to determine the relative value of freshly precipitated copper hydrate as a detoxicating agent. In one test, portions of cod oil were agitated with 5 per cent of freshly prepared copper hydrate, commercial copper carbonate and lead oxide at 180° to 200° C. for two hours. After filtering, these samples were treated with hydrogen, using 5 per cent nickel oxide as a source of catalyzer. This was reduced in oil at 250° C. for one-half hour. The hydrogenation operation was carried out at 230° C. for three hours. The oil treated with freshly precipitated copper hydrate hardened to a melting-point of 53° to 54° C., the oil treated with copper carbonate hardened slightly, while the oil treated with lead oxide did not harden.

553. To determine the most effective temperature for treating the oil with copper hydrate the following tests were performed: Cod oil was agitated with $\frac{1}{2}$ per cent of copper hydrate for one hour at room temperature, then was filtered and subjected to the hydrogenation process. Another portion of the oil was treated in a similar manner, except the temperature of treatment with copper hydrate was 50° C. Other portions were treated at 75° and at 110° to 120° C. The samples treated below 110° C. did not harden and metallic mirrors were formed on the walls of the container during the treatment with hydrogen. The sample which was agitated at room temperature exhibited the most perfect mirror. The oil treated at 110° to 120° C. hardened readily without the formation of a mirror.

554. The effect of refining cod oil with alkali before hydrogenation, when the copper hydrate treatment is used, is beneficial to the catalyzer as was shown by agitating crude cod oil with copper hydrate at 140° to 150° C. for one hour, filtering and then subjecting it to the hydrogenation process, using nickel oxide. The catalyzer was formed in the oil at 250° C. and hydrogenation was carried out at 190° to 200° C. for four hours. The oil was only slightly hardened.

555. A quantity of the oil under examination was burned in oxygen in a combustion bomb. The contents of the bomb were washed out and examined qualitatively. Sulphates and a trace of iodine compounds were found to be present but no test was obtained for either chlorides or phosphates. Either sulphur in the sulphide form or iodine could have been responsible for the poisoning action on the catalyzer noted.

556. Menhaden Oil. Southern crude fish (menhaden) oil, without refining, was subjected to the hydrogenation process, using nickel oxide reduced in the oil at 250° C. and the hydrogen treatment was carried out at 200° C. for four hours. The oil was not hardened. Another

²² U. S. Pat. 1,132,710, Mar. 23, 1915. Cf. 1,247,516, Nov. 20, 1917, to Ellis.

²³ *J. Ind. Eng. Chem.*, 1916, 886.

portion of the same oil was agitated with copper hydrate at 135° to 150° C. for one hour and treated under the same conditions as above. The oil was hardened, without difficulty, to a melting-point of 45° to 46° C. Another quantity of the same crude fish oil was refined and then treated with copper hydrate. The treated oil was hydrogenated, using a catalyzer which had previously been used in cod oil that had been detoxicated with copper hydrate. The oil hardened to a melting-point of 52° to 53° C. The catalyzer was apparently not affected by its previous use in cod oil which had been treated with copper hydrate.

557. Herring Oil which could not be hardened by the usual methods was refined to free it from fatty acids and after treating with copper hydrate for one hour at 110° to 120° C. was subjected to the action of hydrogen in the presence of a catalyzer prepared by reducing nickel oxide in the oil at 250° C. for one-half hour. The oil was hydrogenated at 190° to 200° C. for five hours. It hardened to a melting-point of 45° to 46° C.

558. Dogfish Oil. This oil has proved somewhat difficult to hydrogenate. In one case, a sample of the oil was agitated with copper hydrate for one hour and then treated with hydrogen, using a catalyzer prepared by precipitating nickel hydrate on a carrier and reducing at 360° C. Hydrogenation was conducted for 5½ hours at 180° to 190° C. The oil did not harden. The catalyzer was filtered out and 5 per cent of a mixture of finely divided nickel-copper hydrate was added. A current of hydrogen was passed through the oil, the temperature of the oil being held at 250° C. for one-half hour, then lowered to 190° to 200° C. and maintained at that point for three hours. The oil hardened to a melting-point of 45° C.

559. According to Ueno metallic soaps and other impurities in oils, which act as catalyst poisons during hydrogenation, can be removed by treating the oil with 10 per cent of acid earth (fuller's earth) at 120° C. for twenty minutes. If hardened oils are treated with the acid earth, their content of nickel or other mineral matter is markedly reduced.³⁴

559A. The same investigator ³⁵ reports that to cottonseed, arachis, herring and dab oils, different impurities such as alkali and metallic soap and oxidized acids were added and the oils were treated with a very small amount of an alkali. The oils thus refined contained no ash. Soap solutions will also refine the oil, but their action is much slower than that of an alkali. Various anti-catalyzers of hydrogenation of the oils can also be removed by the same method of refining. Since for the removal of anti-catalyzers the amount of alkali required is far smaller than that required for neutralization of the free fatty acids in oil, for such an industrial hardening as fish oil, where anti-catalyzers should be removed without removal of all free acids, alkali refining is the most advantageous. Ueno believes that alkali refining is accomplished by adsorption of impurities by an emulsoid-like composition formed between alkalies and oils. It is also suggested that in the industrial method of refinement of vitamin-containing fats, if the poisonous matters are first removed by alkali, the activity of vitamins might not be destroyed by subsequent refining treatment.³⁶

560. Oil-hardening catalysts: Influence of Impurities in the Catalyst-carrier.³⁷ An article on this subject is published by Ueno and Saida. The sense

³⁴ *Kogyō-Kwagaku Zasshi* (*J. Chem. Ind., Tokyo*), 1920, **23**, 1028; *J.S.C.I.*, 1920, 825A. See Schwarzkopf, *Brit. Pat.* 138,115, 1920. Oil is freed from free fatty acid by heating with fuller's earth, *in vacuo*, at 250° C.

³⁵ *Ibid.*, 1922, **25**, 578-583.

³⁶ *Chem. Abst.*, 1922, **16**, 4081 (1922); Andrews (*Chem. Trade J.*, 1929, **84**, 277-278, 302-303, 351-352, 369-370) investigated the effect of various oil impurities on the hydrogenation of peanut oil in the presence of a nickel-diatomite catalyst. Addition of 2 per cent of the unsaponifiable matter, or of the stearine separated by freezing from a low-grade, crude cod-liver oil, caused a marked decrease in the rate of hydrogen absorption; a definite decrease in activity of the catalyst also followed the addition of 1 per cent of blood or of 0.3 per cent of lecithin (i.e., 0.02 per cent of organic phosphorus), while hydrogen absorption was completely inhibited by 0.5 per cent of allylthiocarbimide (*cf.*, hardening of rape oils from imported seed). The effect of added isinglass (organic nitrogen) was small and seemed to be physical rather than chemical in nature.

³⁷ Ueno and Saida, *J. Soc. Chem. Ind., Japan*, 1927, **30**, 374; identical abstract in *Chem. Abst.*, 1928, **22**, 879, and *Brit. Chem. Abst.*, 1928, 253A.

is not clear from the abstract, which is given here *verbatim*. "A sample of the kieselguhr was recovered from a spent nickel catalyst by treatment with dilute sulphuric acid and alkali. Nickel catalysts were prepared by using the original and the recovered kieselguhr, and the results were compared. The recovered kieselguhr was as effective as the original material, in spite of the fact that the former contained much impurity, especially calcium sulphate, which would have had a retarding influence on the catalytic reaction. It is concluded that the inhibiting influence of these impurities depends on their existence in the system in a peculiar form."

561. To prevent the formation of catalyst poisons during storage, Lever Bros., Ltd., and Thomas³⁸ add a small quantity of a phenolic substance to the comparatively fresh oil. A fraction of 1 per cent of one or more of the following antioxidant substances is employed: quinol, guaiacol, resorcinol. Oils so treated can be satisfactorily hydrogenated even after prolonged storage or exposure.³⁹

562. Esterification of Free Fatty Acid with Glycerol. The hydrogenation of fatty material containing such quantities of free fatty acids as tend to interfere seriously with the catalytic process is carried out by Ellis⁴⁰ by esterifying the fatty acids with glycerol.

This may be carried out by heating the oil with glycerol to a temperature between 250° and 285° C. for two or three hours. The reaction mass may be kept out of contact with air by introduction of a current of hydrogen. In one case a whale oil having an acid number of about 25 was treated with 5 per cent of glycerol and the acid number was reduced to approximately 1. After the esterification stage has been completed a catalytic agent is added to the oil and the product hydrogenated at a temperature of about 180° C. in the case of nickel or at a lower temperature if a catalyzer of the platinum group is employed.

563. In the same order of ideas is the proposal of Bolton and Lush⁴¹ to prevent inhibition of catalytic hydrogenation due to free fatty acid by the addition of mono- or di-glycerides. These are intended to combine with the free acid, with the formation of triglycerides.⁴²

564. Esterification (ethylation) with Ethyl Alcohol. The application of esterification as a means to reduce free fatty acid has been utilized by Dreyman in the treatment of oils which cannot be readily refined by caustic alkali.

Dreyman states that the presence of even as small a quantity as 2 per cent of free fatty acid in an oil is sufficient to greatly impair the effectiveness of the catalytic agent used in the hydrogenation process. Hence it is the practice to first carefully neutralize the oil by means of caustic soda. If the amount of the free fatty acids exceeds 5 per cent, their removal by caustic alkali refining is difficult and is attended with considerable loss and expense. In consequence, Dreyman states only high-grade neutral oils are being used for hydrogenation purposes. Dreyman proposes to meet the difficulty by esterifying the free fatty acid of the oil with alcohol, which he states can be hydrogenated as readily as a pure glyceride. In this way, oils and fats containing as much as 20 per cent of free fatty acid may be hardened.

³⁸ Brit. Pat. 208,189, Aug. 8, 1922.

³⁹ For antioxidants in general consult articles by Moureu, see para. 387.

⁴⁰ U. S. Pat. 1,261,911, Apr. 9, 1918. See also Nos. 1,271,575 and 1,271,576, July 9, 1918.

⁴¹ Brit. Pat. 162,382, Jan. 27, 1920; *J.S.C.I.*, 1921, 438A.

⁴² Strange to say, in the hydrogenation of herring and cottonseed oils, Ueno (*J. Chem. Ind. Japan*, 1922, 25, 777; *Chem. Abst.*, 1923, 17, 3105) found that palmitic, oleic, stearic and benzoic acids promote the reaction when present to the amount of 2 or 3 per cent. This lacks confirmation.

Applying the process to a fatty oil containing about 20 per cent of free fatty acid, Dreyman recommends the use of 5 to 8 parts of absolute ethyl alcohol to 100 parts of the oil. A small quantity of hydrochloric acid is added to act as a catalyzer in the esterification operation and calcium chloride is introduced to serve as a dehydrating agent. Dreyman recommends 3 parts of hydrochloric acid and 20 parts of calcium chloride. The mixture is heated to a temperature of about 90° C., for three hours, after which time the product is washed with water and will then be found to have a low content of free fatty acid, in general, less than 3 per cent. This amount of free fatty acid can be readily removed by the caustic soda refining process. When the oil or fat contains 30 per cent or more of free acid, Dreyman states it is advantageous to remove the glycerol as, for example, by the Twitchell process. The fatty acids thus obtained can be converted into esters by treatment with alcohol, the proportion of alcohol in this case being increased to 20 parts. He states that the esters thus produced contain only 1 to 3 per cent free fatty acid, which may be removed by refining with alkali. The application of the process to the treatment of inferior products, such as cotton oil, soap stock, and garbage grease, is recommended.⁴³

565. Esterification with Glycol. According to Schlinck, the neutralization of the undesirable free fatty acids is effected by esterification with glycol.⁴⁴ The oil is heated with glycol for several hours under a reflux condenser, the water formed is removed by a current of inert gas. (The condenser must, therefore, maintain a temperature above 100° C.) In a modification of this method⁴⁵ the glycol esterification and the catalytic hydrogenation are described as being carried on simultaneously.

566. Purification by Distillation. In the hardening industry purification by distillation of the material to be hydrogenated (or substrate) can be applied only to free fatty acids, because the glycerides cannot be distilled, without decomposition, except *in vacua* of so high a degree as to be unattainable in practice.

De Roubaix⁴⁶ reports that commercial oleic acid may be completely hydrogenated, after purification by distillation under diminished pressure, by means of a rapid current of hydrogen at atmospheric pressure in the presence of 4 per cent of reduced nickel as catalyst, the temperature being between 160° and 230°. The catalyst should not be prepared within the material to be hydrogenated, as this leads to considerable formation of nickel oleate, which De Roubaix considers encloses the nickel particles and inhibits their action. The presence of sulphur in non-distilled olein poisons the catalyst.⁴⁷

RELEVANT REFERENCES

567. Bakh. Mechanism of poisoning of catalysts. *Trans. Karpov Inst. Chem.*, 1925, No. 4, 11. An examination of the reaction $\text{NaH}_2\text{PO}_2 + \text{H}_2\text{O} = \text{NaH}_2\text{PO}_3 + \text{H}_2$, catalysed by palladium, to determine whether definite or infinitesimal quantities of poisons are required to destroy the activity of the catalyst. With palladium-black, the quantities of various poisons required for 1 mol. of palladous chloride were: potassium cyanide, 1.75 mol., mercuric chloride, 1 mol., thiocarbamide, 1.5 mol., quinine hydrochloride, more than 10 mols. Alkaloids generally have a relatively weak action on catalysts. The poisoning effect is due partly to chemical combination between the palladous chloride and the poison, yielding a compound which cannot be reduced by sodium hypophosphite, and partly to adsorption on the surface of the palladium-black. With colloidal palladium, the effect is one of adsorption, and again a definite number of mols of the poison is required to saturate the surface of the palladium particles and paralyze their action.⁴⁸

⁴³ U. S. Pat. 1,228,888, June 5, 1917.

⁴⁴ Ger. Pat. 315,222, June 11, 1916; *J.S.C.I.*, 1920, 198A.

⁴⁵ Ger. Pat. 334,659, Aug. 15, 1916.

⁴⁶ *Bull. soc. chim. belg.*, 1924, 33, 193.

⁴⁷ Cf. paras. 4035 and 4036 (Starrels' patents).

⁴⁸ *Chem. Abst.*, 1926, 20, 2272.

568. Constable. Sintering of active copper catalysts. [*J. Chem. Soc.*, 1927 1578.] Results are said to confirm the views of Pease and Constable rather than those of Taylor and of Armstrong and Hilditch.

Idem. An auto-poisoning⁴⁹ phenomenon shown by catalytically active copper at moderate temperatures, *Ibid.*, 2995. Notwithstanding purity of reactants and the use of a temperature at which catalytic copper surfaces are stable, copper used as catalyst in the dehydrogenation of alcohol decays in activity.

569. Griffin. Adsorption of hydrogen and ethylene by copper catalyzers with simultaneous poisoning by carbon monoxide. [*J. Am. Chem. Soc.*, 1927, 49, 2136.]

Experiments were made on the adsorption of hydrogen and ethylene on copper catalysts in presence of small amounts of carbon monoxide. The carbon monoxide was introduced in calculated amounts before the beginning of the experiment. The hydrogen or ethylene and carbon monoxide were determined at 0° and 20° after each experiment, and the adsorption of all three gases was measured on pure catalysts beforehand. For low pressures the adsorption values of ethylene and hydrogen rise in presence of carbon monoxide; at high pressures adsorption falls. Griffin suggests that carbon monoxide tends to stimulate the forces of adsorption at the active points. Because of the low critical temperatures of the gases, there can be no question of capillary condensation; hence it must be assumed that an adsorbed carbon monoxide molecule has the power of holding to itself several hydrogen or ethylene molecules, either in itself or by strengthening adjacent centers of activity.

570. Maxted. The influence of hydrogen sulphide on the occlusion of hydrogen by palladium. *J. Chem. Soc.*, 1919, 115, 1050; 1920, 117, 1280.

Maxted. The influence of lead on the catalytic activity of platinum. *J. Chem. Soc.*, 1920, 117, 1501.

Maxted. The influence of mercury, sulphur, arsenic, and zinc on the catalytic activity of platinum. *J. Chem. Soc.*, 1921, 225.

571. Paal and Hartmann. Influence of foreign substances on the activity of catalysts. *Ber.*, 1918, 51, 894. Poisoning of palladium hydrosol for catalysis of detonating gas. Mercury and its oxide permanently poison the catalyst. Precipitated and colloidal copper hydroxide cause progressive poisoning, though the quantities tested did not cause complete paralysis. Precipitated zinc oxide at first partially inhibits the catalysis, then regeneration occurs with restoration to at least original activity.⁵⁰

572. Watanabe. Poisoning effect of certain substances on the iron catalyst in the decomposition of carbon monoxide. *Bull. Inst. Phys. Res. (Tokyo)*, 1928, 7, 1078; *Abstracts*, 1, 102; *Chem. Abst.*, 1929, 23, 1560. The substances tested for their effect on the catalyst were: water, nitrogen, hydrogen, methane, acetylene, benzene, naphthalene, hydrogen sulphide, thiophene. Acetylene liberates carbon but has no other effect. Water causes the formation of carbon dioxide, hydrogen and methane. Naphthalene causes a progressive decrease of activity, but pure carbon monoxide restores the catalyst to full activity. Sulphur compounds permanently poison the catalyst.

⁴⁹ "Auto-poisoning" is a repulsive hybrid word, but a better one is difficult to find: "auto-intoxication" has a fixed connotation; "self-poisoning" suggests suicide, and is also hybrid.

⁵⁰ Bredig, *Ber.*, 1918, 51, 1477, points out that he and von Berneck, *Z. physik. Chem.*, 1899, 31, 327, had reported the poisoning of a platinum catalyst by mercury.

CHAPTER VI

PROMOTERS AND CO-CATALYSTS

PROMOTERS

600. Normally the acceleration produced by a catalyst is proportional to the amount of catalyst. It was therefore reasonable to expect that when two similarly acting catalysts were used the resulting acceleration would be the sum of the effects known to be produced by the respective quantity of each catalyst acting separately. Thus if 1 per cent of a metal, under given conditions, catalyzed a certain hydrogenation reaction so that the operation was complete in six hours, and if 0.25 per cent of another metal, in the same conditions, produced the same effect in thirty-six hours, it might be predicted that 1 per cent of the first metal plus 0.25 per cent of the second metal would bring the hydrogenation to an end in a little more than five hours. Such expectation is often realized approximately, but, in a great many instances, the acceleration is increased in a wholly disproportionate degree.

601. This surprising result, of which no wholly adequate general explanation has been offered, is called Promoter Action. The secondary catalysts which produce it are known as Promoters. They have become of much importance in industrial catalysis.

602. Pease and Taylor¹ define promoter action as including all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present. Three cases are distinguished:

- (1) Activation of a catalyst by a relatively inert substance.
- (2) Activation of a catalyst by a small quantity of a relatively active substance.
- (3) Co-activation of a number of catalysts, each by the others.

603. Ipatiev found that copper oxide in an iron tube was more active in the hydrogenation of amylene than was copper oxide in a copper tube. The Badische Company state that hydrogenation of fats with nickel is promoted by the presence of tellurium. Dewar and Liebmann claim that a mixture of nickel and copper oxides can be reduced in the oil at 190° and will hydrogenate cottonseed oil rapidly at that temperature, whereas nickel oxide alone requires a temperature of about 250° for reduction. Hochstetter found that a mixture of silver and copper was more effective for the synthesis of formaldehyde from methanol than either metal singly.²

¹ *J. Phys. Chem.*, 1920, **24**, 241; contains a useful review of the subject up to 1920.

² First report of the Committee on Contact Catalysis, 1922, p. 16.

604. Russell and Taylor³ in a study of the reaction $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ found that, in this reaction, when it is catalyzed by nickel, the presence of thoria causes a decided promoter effect. Now the higher the temperature at which nickel catalyst is reduced the lower its activity. Russell and Taylor, having in mind Taylor's conception of a solid catalyst surface (see para. 217), view this effect of high temperature as due to the collapse of the "high points" of that surface, owing to the increased mobility of the atoms which coalesce, with loss of effective adsorptive power. The thoria promoter effect may be due to any or all of the following: (1) by creation of thoria-nickel interfaces the number of unsaturated nickel atoms is increased; (2) as a support thoria increases the catalytic surface; (3) thoria may influence, favorably, the adsorption ratio of the reactants and, possibly, of the reaction products.

605. Alumina: Carrier Function. Rosenmund and Joithe⁴ examined the rôle of alumina as a carrier or co-catalyst. In particular they considered the reduction of borneol to isocamphane by a nickel or nickel oxide (*sic*, Ipatiev) primary catalyst on alumina. The rôle of alumina is thought to be (1) adsorption bringing the reactant to the nickel; (2) dehydration. These investigators extend this explanation to the promoter actions of thoria and titania.

606. Zelinsky and Kommarevsky⁵ have also studied a catalyst composed of nickel on aluminum hydroxide. They contrast its action with that of nickel and find that it is more like a catalyst of the platinum group. In other words, the experimental results would seem to confirm the view that the aluminum hydroxide is a promoter, or a modifier, or a co-catalyst, at any rate, not a mere inert extending medium.

607. Smith⁶ investigated the catalytic effect in the synthesis of water between 75° and 180° with an oxygen concentration of 2.4 per cent, of the following catalysts, prepared by reduction of the precipitated hydroxides, copper, nickel, copper-nickel mixtures, a mixture of copper and alumina. Copper prepared by reduction of the fused oxide was also used. The most efficient catalysts were those which formed the greatest amounts of oxide during catalysis and underwent the least change in physical structure, especially shrinkage, on reduction and later heat treatment. Precipitated copper, which shrinks most during its preparation, is the worst catalyst.⁷ The order of decreasing catalytic efficiency is copper-alumina (19:1), copper from the fused oxide, nickel, nickel-copper (1:3), copper-nickel (1:7.5), and copper from the precipitated hydroxide. Heating to 444° is accompanied by shrinkage of the catalysts, a decrease in oxide-forming capacity, and, except in the case of nickel, a corresponding decrease in catalytic efficiency. These effects were slight with the copper-alumina catalyst and large with the precipitated copper. The behavior of the nickel may be explained by the changes in physical properties accompanying the transition temperature at 360°. The results show that the physical nature of the catalyst surface, as well as its chemical properties, is of prime importance in determining catalytic activity, and they agree with Taylor's theory of a catalytic surface. The probable mechanism appears to consist of the interaction of hydrogen molecules and activated oxygen molecules or atoms, in the form of an oxide, at points of greatest activity on the surface of the catalyst. The stable oxide formed seems to play little part in the synthesis. It is formed by an unavoidable side reaction which ultimately results in a partial poisoning of the catalyst.⁸

608. Medsforth⁹ inclines to the view that the usual function of promoters is to adsorb preferentially one of the reactants for which the main catalyst has insufficient adsorptive power in the conditions present, to produce a concentration ratio favorable to the reaction. Nevertheless he puts forth as possible explanations of some promoter effects: (1) The decomposition of "intermediate compounds"; (2) the formation of intermediate complexes with reactants which are then broken up by the primary catalyst with the production of new compounds.

609. Armstrong and Hilditch,¹⁰ on the other hand, find in the increase of catalyst surface a sufficient explanation of most promoter actions. This would,

³ *J. Phys. Chem.*, 1925, **29**, 1325; *Chem. Abst.*, 1926, **20**, 325. The abstract is full.

⁴ *Ber.*, 1925, **58B**, 2054; *Chem. Abst.*, 1926, **20**, 751. This abstract is unusually complete.

⁵ *Ber.*, 1924, **57B**, 667.

⁶ *J. Phys. Chem.*, 1928, **32**, 719.

⁷ Cf. Armstrong and Hilditch, *Proc. Roy. Soc.*, 1921, **99A**, 490.

⁸ *Brit. Chem. Abst.*, 1928, 719A.

⁹ *J. Chem. Soc.*, 1923, **123**, 1452; *Idem*, *J.S.C.I.*, 1923, **42**, 423.

¹⁰ *Proc. Roy. Soc.*, 1923, **103**, 25.

naturally, not be applied to selective promotion, of which many instances are known.

610. The extension of the catalyst surface is not merely a question of area. It may be asserted, with confidence, that a square meter of catalyst in plane form, recently fused ("fire-polished") would display less catalytic activity than the same area of subdivided catalytic material. The latter has, in the first place, sharp curves and in the second place, more interfaces: both these characteristics are important in the relation to enhanced catalytic activity.¹¹

611. There is a considerable body of opinion to the effect that one important function of promoters is performed once for all during the preparation of the catalyst. This is the prevention of sintering, which would be accompanied by the diminution, not only of total surface, but also of the more important active points from which atoms would migrate to points of less free energy.

612. Reciprocal Excitation and Inactivation of Catalysts. Quartaroli¹² has examined the influence exerted by certain substances when present in catalyzed reactions, and finds that the same substance may act in one reaction as a retarding agent, and in another, similar reaction as an accelerator. For example: nickel, cadmium and magnesium hydroxides retard the decomposition of alkaline hydrogen peroxide and, similarly, reduce the power of lead hydroxide to accelerate the decomposition of hydrogen peroxide. But these same agents greatly accelerate the decomposition of hydrogen peroxide by oxide of silver.

MIXED CATALYSTS

MIXTURE OF METALS

613. Hitherto we have treated of hydrogenation catalysts as composed of single metals. In practice, however, they are often mixtures of metals. A catalyst composed of nickel with a small percentage of copper is of considerable importance in the fat hardening industry. The second metal is usually known as a promoter, though sometimes called an auxiliary or co-catalyst.

614. Dewar and Liebmann¹³ are among those who, rather early in the development of the hydrogenation of oils in the liquid state, availed themselves of such auxiliary catalysts. Heated oils were subjected to treatment with hydrogen in the presence of a mixture of the hydroxides, oxides, or carbonates of nickel, copper and cobalt, or of these compounds with palladium, platinum, silver, or silver oxide.

615. Mutual Activation of Inactive Platinum Metals. Some rather remarkable results are reported by Remy and Schaefer.¹⁴ They compared the activity of platinum metals and their alloys in catalyzing the union of hydrogen and oxygen at room temperature. A moderately active metal had its activity much enhanced by alloying with an inactive metal and an alloy of two inactive metals was highly active.

616. Copper as Promoter or Co-catalyst with Nickel. According to Armstrong and Hilditch¹⁵ a copper-nickel catalyst may be reduced in hydrogen when mixed

¹¹ Rideal and Taylor, *loc. cit.*, 108-109.

¹² *Gazz. chim. ital.*, 1927, **57**, 234; *Chem. Abst.*, 1927, **21**, 2088.

¹³ *Brit. Pat.* 12,922, 1913; *Chem. Abst.*, 1916, 284; *J.S.C.I.*, 1915, 797.

¹⁴ *Z. anorg. allgem. Chem.*, 1924, **136**, 149; *Chem. Abst.*, 1924, **18**, 3307.

¹⁵ *Proc. Roy. Soc.*, 1922, **A102**, 27.

compounds of copper and nickel distributed on suitable carriers are heated to 180° C., whereas nickel compounds alone under such conditions are not reduced by hydrogen below 300° C. and not rapidly below 350°–400° C. For the reduction of nickel at this low temperature an intimate mixture of the copper and nickel compounds must be used, which must be more intimate than can be obtained by mechanical mixing. Co-precipitation is not always sufficient to obtain the desired degree of intimacy, for a comparison of the activity of the catalysts with the nature of the nickel cupric carbonates from which they are produced shows that both the nickel and the copper must be in the same complex molecule to obtain any marked degree of catalytic activity. It is suggested that the necessary local heat to provide a sufficiently high temperature for the reduction of the nickel is furnished by the reduction of the copper, provided the latter is in sufficiently close proximity to the nickel.¹⁶

617. Kayser¹⁷ refers to the use in catalytic processes, of nickel compounds, such as the carbonate, hydrate, oxide, formate or acetate and to the effect of auxiliary catalysts.

618. Excessive heating of all but a limited quantity of fatty material may be avoided, in the practice of fat-hardening, by preparing a concentrated fatty catalyzer-paste or catalyzer-cake, which is thereafter used at a lower temperature for the conversion of unsaturated fatty bodies in presence of hydrogen; or the preliminary treatment of the catalyzer stock may be carried out at relatively high temperatures in another medium, such as paraffine wax, the resulting catalyzer being thereafter isolated. These methods, however, are stated to be not without inconvenience and drawbacks. Kayser observes that these nickel compounds, and some others not hitherto available, can readily be converted into catalysts of superior activity and longevity, and this at a temperature not exceeding 180° C., when the preliminary treatment is carried out in presence of a small quantity of certain finely divided metals, and that fatty bodies can, at a moderate temperature, be conveniently saturated with hydrogen to any desired degree if they are submitted to the action of hydrogen in the simultaneous presence of the usual amount of nickel compound and of a comparatively small amount of finely divided auxiliary catalytic metal, such as would by itself exercise upon the fat but very slight action, or no action whatever.

619. Thus, if cottonseed oil be agitated with hydrogen at 180° C. in presence of about 2.5 per cent of commercial nickel carbonate, the mixture does not change color, and no hardening of the oil takes place. If the oil be similarly treated with the gas in the sole presence of about $\frac{1}{2}$ g. of so-called "atomic" copper, prepared by the action of zinc dust on copper sulphate solution, a like negative result is registered. If, however, quantities of nickel carbonate and copper metal be simultaneously present, the charge rapidly darkens and becomes progressively hardened, showing after two hours a melting-point of 46° C., after three hours, 52° C., and after four hours, 56° C. When finally freed from suspended catalyzer by filtration or other mechanical means, the fat will set to a white, tasteless and odorless, brittle solid. The recovered catalyzer can repeatedly be used in the same manner; its activity will at first be found to increase and then to slowly decline. Similar, but somewhat inferior, results are stated to be produced with nickel hydrate in place of carbonate, while the oxides and organic nickel salts do not readily cooperate, or entirely fail, with copper. Such organic compounds, as the formate, on the contrary are, like the hydrate, the carbonate and the oxide of nickel, rapidly transformed and activated by a small quantity of catalytic metallic nickel, produced by dry reduction of the oxide, hydrate or carbonate in a current of hydrogen. Even the oxalate, otherwise quite stable, at 275° C. is said to be readily transformed into an efficient catalyzer. For example, 250 g. of cottonseed oil, agitated with hydrogen at 180° C. in presence of 3.5 g. of active nickel-powder, are in three hours hardened to a melting-point of 37° C.; in the simultaneous presence of 7 g. of nickel hydrate the charge rapidly turns grey and, when

¹⁶ *J.S.C.I.*, 1922, 41, 903A. See para. 625 for a copper-nickel catalyst reduced from co-precipitated formates below 200° C.

¹⁷ U. S. Pat. 1,236,446, August 14, 1917.

filtered after three hours running, yields a white fat, melting at 45° C. In the same manner, cooperation of 0.5 g. nickel-powder with 12.5 g. nickel oxalate yields in three hours a white fat, melting at 54° C. The reactions described may frequently be facilitated by using, instead of the pure nickel compound and the pure auxiliary metal, the like bodies, deposited upon kieselguhr or a similar indifferent support. The chemical nature and the appearance of the catalyzer produced by the process, varies with the auxiliary metal employed. Nickel is stated to yield a grey, non-metallic catalyzer, while copper produces a black body, developing with hydrochloric acid far less hydrogen than what would correspond with the hypothetical sub-oxide Ni_2O .

620. Mixed Metal Catalyst Containing Platinum. A catalyzer used in the production of propylene by the union of acetylene and methane and containing two catalytic metals is prepared by Heinemann in the following manner:

621. One of the contact metals, for example, copper, is deposited in a porous body, for example, pumice stone, either electrolytically, or by the reduction of a copper salt. The pumice stone, provided with a coating of copper, or having its pores partly filled with copper, is dipped in a solution of a salt of a contact metal of the platinum class, for instance, chloride of platinum, and is dried. The salt is then reduced. In this way there is obtained a contact body consisting of two metals which are stated to exert a mutual balancing effect on one another, the more active property of the platinum group metal being mitigated by the less active property of the other metal associated therewith, allowing the desired reaction to take place at a moderate temperature.¹⁸

622. Ellis¹⁹ described the preparation of a mixed metal catalyst, containing nickel as the principal and a small percentage of copper as the auxiliary component, by reduction of the mixed hydrates in heated oil or glycerol. This nickel-copper catalyst is recommended especially for the hydrogenation of fish oil, and is considered to be more active than a simple nickel catalyst in the hydrogenation of oleic acid. This is one of the most extensively used industrial hydrogenation catalysts.

623. Ellis also has proposed to make a mixed catalyst by heating mixtures of organic salts (e.g., oleates) of nickel, cobalt and copper in oil with or without a current of hydrogen.²⁰

624. According to Patel²¹ the presence in nickel-kieselguhr catalysts of cobalt, silver or copper has an inhibiting effect on the hydrogenation of oils. For copper and cobalt, at any rate, this statement should not be accepted until corroborated.

625. Catalyst from Mixed Nickel and Copper Formates. In the type of catalyst made by reduction of nickel formate by heating with hydrogen in the presence of oil the temperature of reduction is much lowered (below 200° C.) by the presence of 10 to 20 per cent of copper formate. This avoids production of oil exhibiting a burnt taste or odor.²²

626. A somewhat original line of catalysts for the hydrogenation of cottonseed oil was described in 1921 by Kahlenberg and Ritter,²³ though no industrial use of them seems to have been disclosed since that time. They reported that while nickel was the best single catalyst, a mixture of nickel and cobalt in equal parts was better than either metal alone; zinc carbonate, freshly precipitated in presence of aluminum powder, was a fair catalyst; bismuth precipitated on charcoal and reduced with hydrogen at 350° C. was also fairly active. Two other nickel catalysts were described: (1) nickel deposited on arsenic-free zinc from a saturated solution of nickel chloride, this was found to catalyze the hydrogenation of the oil at atmospheric pressure and at low temperatures; (2) nickel chloride reduced with hydrogen at 180°-250°, this works fairly well at 170° C.

¹⁸ U. S. Pat. 1,202,385.

¹⁹ U. S. Pat. 1,156,068, Oct. 12, 1915.

²⁰ U. S. Pat. 1,378,338.

²¹ *J. Indian Inst. Sci.*, 1924, 197; *Chem. Abst.*, 19, 740.

²² U. S. Pat. 1,645,377, Oct. 11, 1927, to Ellis.

²³ *J. Phys. Chem.*, 1921, 25, 89; *Chem. Abst.*, 1921, 15, 1411.

627. Sulzberger²⁴ reduces nickel compounds in the wet way (e.g., by use of hydrazine) in presence of a small quantity of an "inciter" (e.g., compound of palladium). The presence of the latter increases catalytic activity. The product is not pyrophoric, but is active. It clarifies readily from oil.

628. The same investigator²⁵ prepares a catalyst, for hydrogenation of oil, which is essentially a mixture of nickel, cobalt or uranium as principal catalyst with platinum or palladium. An aqueous solution of nickel sulphate with 0.1 per cent of platinum is treated with hydrazine sulphate and heated with an excess of sodium hydroxide. A black precipitate is thrown down. This is an active non-pyrophoric catalyst.²⁶

629. One variation of Schuck's method of preparing catalyst by atomizing a mixed solution of metal nitrate and sugar through a muffle, uses a solution containing two metals, one being nickel.²⁷

630. Hagemann and Baskerville's method for the use of "tarnished shapes" of nickel as catalyst²⁸ prescribes the use of an alloy containing a small percentage of cobalt.

METAL CATALYST WITH NON-METAL PROMOTER

631. When a metal catalyst is used in combination with a non-metal it is not always possible dogmatically to class the latter either as a promoter or as an inert carrier. Sometimes it seems to play both rôles and often it is difficult to say which is its primary function. This chapter must, therefore, somewhat overlap with the next which deals with "inert" carriers.

632. The *locus classicus* for non-metallic promoters is in a series of patents taken out by the Badische Company from 1910-1914.²⁹

633. The Badische Co.³⁰ report that the hydrogenation and dehydrogenation of compounds containing carbon can be carried out rapidly and at comparatively low temperatures, by employing, as the catalytic agent, an intimate mixture of either iron, nickel, cobalt, or copper, with a high melting and difficultly reducible oxide, in particular, the oxides and oxygen salts of the earth metals, including the rare earths, and those of beryllium, magnesium, manganese, uranium, vanadium, niobium, tantalum, chromium, boron, titanium and also difficultly soluble phosphates, molybdates, tungstates and selenates of the alkaline earths, and of lithium, or the reduction products, containing oxygen, of these phosphates, molybdates, tungstates, or selenates, as for instance, the corresponding selenites: all of these compounds containing oxygen, which augment the activity of the catalytic agent, are termed "promoters" (the name is no longer limited to oxygen-containing compounds).

634. The oxygen-containing salts of the alkaline earths and of lithium appear to have the same action as the corresponding salts of aluminum, magnesium, and the like, although lithium oxide and the oxides of calcium, barium, and strontium are themselves not suitable for use as promoters. An intimate mixture of the catalytic metal and a promoter is required and it is not sufficient, according to the Badische Co., merely to pack the components, for instance, nickel and alumina, side by side, into the reaction space, nor is it adequate to absorb

²⁴ U. S. Pat. (reissue) 1,164,141, May 27, 1919.

²⁵ Sulzberger, U. S. Pat. 1,426,517, Aug. 22, 1922; Canad. Pat. 181,447, 1918.

²⁶ *Chem. Abst.*, 1922, 16, 3768; *ibid.*, 1918, 605.

²⁷ *Chem. Abst.*, 1920, 1228.

²⁸ See para. 1051.

²⁹ See: Rideal and Taylor. *Catalysis in Theory and Practice*, 2d ed., p. 38.

³⁰ Brit. Pat. 2306, 1914.

a solution of a salt of the catalytic metal into a porous mass, such as magnesia, and then decompose the salt of the catalytic metal. Good results can be obtained by precipitating the hydroxides, oxides, or carbonates, of the components; or mixtures of salts, for instance, the nitrates of the components, can be heated to fusion. Further, it is stated that the mixture can be obtained, although not always with equal certainty and excellence, by mechanical operations, such as by grinding together as finely as possible, or by kneading in a moist state. If necessary the mixture is subsequently heated and reduced so that the catalytic metal (iron, nickel, cobalt, or copper), is obtained in a metallic condition, while the promoter always retains more or less oxygen. When the promoter is to consist of an insoluble oxide such, for instance, as aluminum oxide and titanium oxide, it is preferred to start with a soluble compound, and to precipitate, or otherwise form the insoluble oxide on the catalytic metal, or on the compound from which the catalytic metal is to be prepared. For instance, if aluminum acetate be employed to yield the promoter, aluminum oxide, the acetate can be merely heated in the presence of the catalytic metal, or a compound of the latter, so that the acetic acid is driven off, and the alumina remains. If insoluble salts, such, for instance, as certain chromates and borates, be employed as promoters, these are preferably brought into intimate mixture with the compound, which is subsequently to give rise to the metallic catalytic agent, by precipitation from suitable soluble salts. The salts which act as promoters may contain the oxide, to which the promoting action is ascribed, either in the acid constituent, or in the basic constituent, or in both the acid and basic constituents. Calcium aluminate and aluminum phosphate are instances of compounds of this character. In some cases the promoter may consist of a salt, of which neither the acid constituent nor the basic constituent of itself acts as a promoter. Calcium phosphate is an example of this type.

635. It is particularly advantageous for the purpose of producing a very active contact mass to prepare, at least the catalytic metal, from carbonaceous salts, or mixtures of salts; for instance, from carbonates or from formates. Sometimes the action of the catalytic mixture, it is alleged, can further be increased by adding an alkaline metal compound, for instance, caustic soda, even traces of such bodies often having a favorable action. The introduction of bodies such as chlorine, sulphur, arsenic, and lead, which may, in the elementary form, act as contact poisons, is to be avoided, although these contact mixtures are claimed to be not so sensitive to the action of poisons as are the pure metals. It is consequently possible to employ as a promoter an oxygen salt which contains one of the poisonous elements, but in which the poisonous action is counteracted by the promoting influence of the oxide; for instance, basic aluminum sulphate is observed to possess a strong promoting action. The proportion of the components employed in the catalytic mixture may be varied considerably, even an addition of 1 per cent, or less, of the promoter is stated to produce in most cases, favorable action. These catalytic mixtures can be used for the hydrogenation and dehydrogenation of compounds containing carbon and are claimed to be of particular value for the hardening of fats and fatty acids, but they can also be used for other purposes, for instance, for converting phenol into cyclohexanol and for reducing nitrobenzene to aniline, and for the conversion of oxides of carbon into hydrocarbons. The use of mixtures containing strongly basic bodies in the hydrogenation of fats is undesirable. The presence of strong bases is, in such cases, detrimental, since they tend to saponify and very soon disappear from the contact mass.

636. The following are examples of how catalysts can be prepared according to the foregoing, and how they are applied in the hydrogenation of organic bodies. The parts are by weight.

1. Pour an aqueous solution of 1 part aluminum nitrate over 5 parts of nickel oxalate. Evaporate the mixture and dry it and reduce it in a current of hydrogen at from 300° to 350° C. Then introduce the catalyzer, while excluding air, into a vessel provided with a stirrer, the vessel containing fish oil. On treatment with hydrogen at, for instance, 100° C., hydrogenation takes place considerably more rapidly than if pure nickel were employed as the catalytic agent. Instead of aluminum nitrate, cerium nitrate, or cerium ammonium nitrate, can be employed.

2. Precipitate a hot solution containing nickel nitrate and aluminum nitrate with potassium carbonate, wash and dry the precipitate, heat it to 300° C., and reduce with hydrogen. Then place the catalytic mixture with soya-bean oil in an autoclave, while avoiding the presence of air, heat to 80° C. and allow hydrogen to act at a pressure of 20 atmospheres while stirring the constituents. The hydrogenation takes place very rapidly. If desired the pressure can be increased, for instance, up to 50 atmospheres, or higher. In this example, good results can also be obtained if iron nitrate be employed instead of nickel nitrate.

3. Mix 13 parts of nickel hydroxide with 2 parts of magnesium hydroxide, and warm gently with concentrated formic acid free from sulphur, until the formates are obtained. Heat the mixture cautiously until dry, and then treat with hydrogen at 300° C. On treating olive oil with hydrogen in the presence of this catalytic mixture at say, from 80° to 100° C., hydrogenation is effected more rapidly than is the case when pure nickel is used. In this example the hydroxides can, if desired, be replaced by the corresponding carbonates. Carriers such as pieces of clay can be employed, these being soaked in a melt, or solution, of nickel salts, preferably of the soluble double salts, such as nickel ammonium formate, or ammoniacal nickel carbonate, together with similar salts of the promoter, and then treated as described.

4. Make nickel wire netting into the form of loose spheres or rolls, clean these with pure dilute nitric acid, wash and moisten them with a moderately concentrated solution of aluminum nitrate; then dry and treat with hydrogen at from 300° to 350° C. The contact mass containing alumina can, for instance, be employed for the hydrogenation of linseed oil which can be allowed to trickle over the catalytic agent while the hydrogen is supplied.

5. Dissolve 85 parts of nickel nitrate and 15 parts of titanium lactate in a small quantity of hot water and precipitate by means of caustic soda, or sodium carbonate, then filter, wash, dry, and reduce with hydrogen at 300° C. and add the catalytic mixture containing titanium oxide to cottonseed oil, and treat with hydrogen at from 100° to 120° C., while keeping the mixture in motion. If desired the reaction can be carried out under increased pressure (for instance, 100 atmospheres) and in this case the hydrogenation takes place very rapidly and completely, even at a temperature of 90° C. or lower. Further, the process can be made continuous by allowing the oil to flow over the catalytic agent in a vessel capable of withstanding pressure while simultaneously passing a current of hydrogen into, or through the apparatus. The product is drawn off while hot and allowed to solidify.

6. Take freshly precipitated nickel carbonate and add from 10 to 20 per cent of its weight of ammonium or potassium borate, which has previously been dissolved in water. Then form the mass into any desired shape, and dry and reduce it. The mixture can be employed for hydrogenating oils and fats, either at ordinary pressure or under increased pressure. If chromium oxide be used as the promoter, this can be obtained, for instance, from chromium nitrate, or from soluble chromates, by precipitation. Further, when boron oxide is employed as the promoter, the oxide, or carbonate, of the catalytic metal may be mixed with solid, or dissolved, boric acid and then be heated and reduced; or the salt of the catalytic metal, for instance, the nitrate, can be mixed with the borate of the same metal, or of a volatile or non-volatile base, and the mixture is then calcined and reduced.

7. Add 2 parts of dissolved potassium aluminate to a solution containing 30 parts of nickel nitrate and 1½ parts of calcium nitrate and introduce the whole into a boiling solution of sodium carbonate. Then filter, wash well, dry and reduce. Or add a solution of 1½ parts of magnesium nitrate to 5 parts of nickel carbonate, and then add a solution of ½ of a part of ammonium phosphate and precipitate with caustic soda, or sodium carbonate, filter, wash, dry and reduce. The nickel catalytic agent containing calcium aluminate, or magnesium phosphate, as the case may be, can be employed for hydrogenation purposes, for instance, it may be introduced into oil which results from cracking petroleum residues and which is rich in unsaturated compounds, whereupon hydrogen is allowed to react at a temperature of 100° C. and at a pressure of 80 atmospheres. The iodine number is rapidly reduced and at the same time the color and unpleasant odor diminish.

In a similar manner other contact mixtures can be employed, which contain as a promoter, for instance, calcium vanadate, barium chromate, aluminum borate, barium tungstate, or lithium phosphate, or the compounds which result on the reduction of these bodies.

8. To a hot solution of 13 parts of nickel nitrate and 2 parts of chromium nitrate, add a hot solution containing 6 parts of anhydrous sodium carbonate. Filter off the precipitate, wash it until the filtrate is free from alkali, then dry and reduce it. With the help of this catalytic agent, soya-bean oil can be hydrogenized rapidly at a low temperature.

9. Suspend 40 parts of nickel carbonate in a solution containing 1 part of ammonium tungstate and then add a solution of 1 part of barium nitrate, filter off the product, wash it well, dry and reduce it at 300° C. The product can be employed, for example, for hydrogenating sesame oil at 120° C.

10. Mix to a paste 50 parts of nickel carbonate and a solution of 13 parts of calcium nitrate and then stir in a solution of 7 parts of ammonium phosphate. Filter off the product, wash well, dry and reduce at from 300° to 350° C. The product can be employed for hydrogenating fish oil.

11. Stir 80 parts of nickel carbonate into a solution of 2.6 parts of strontium nitrate, and add a solution of 2 parts of ammonium selenite. Filter off the product, wash well, dry and reduce. The product can be used for hydrogenating cottonseed oil.²¹

637. The continuous hydrogenation of unsaturated fatty acids or esters may be carried out according to the Badische Co.²² in the following manner: As a catalyzer is employed nickel, copper, iron, or a mixture of these metals with one another or with agents promoting the activity of the catalyzer. The process is effected under pressure of at least 30 atmospheres and preferably over 50 atmospheres, the catalyst being supported in the pressure vessel so as not to mix with the substance treated. The preparation of the catalyzer may be accomplished by reduction of an oxygen compound of the metal by means of hydrogen under pressure in the same apparatus used for the hydrogenation of the fatty acid, etc. According to examples: finely divided nickel, prepared by reduction of the oxide or carbonate at a low temperature, is supported on a carrier in the pressure vessel, or nickel pieces or wire netting is suitably held therein. Cottonseed or linseed oil is passed into the vessel and treated with hydrogen at 100° under a pressure of 120 atmospheres. Nickel carbonate or formate mixed with alumina and formed into balls or spread on a carrier, is placed on perforated trays in a cylindrical high-pressure apparatus and reduced at 220° to 250° by means of hydrogen under pressures of 30–100 atmospheres. The reduced metal is allowed to cool in hydrogen under a pressure of 30–100 atmospheres. When cooled to about 80°, a stream of the oil to be hydrogenated and hydrogen under pressure are introduced into the apparatus.

638. Kita and Mazume²³ studied the effect of various substances upon the activity of a metallic nickel catalyst in the hardening of soya-bean oil (iodine value 130) at 170° C., the quantity of the added substance being 2–16 per cent (increasing by 2 per cent) of the nickel and the time of reaction 1.5 hours. The substances used were aluminum hydroxide, calcium and magnesium phosphates, magnesia, calcium borate, stearic and palmitic acids (iodine value 7.3 and 2.0), and sodium carbonate, and they were either mixed with the metallic nickel or mixed with nickel oxide or hydroxide and the nickel compound then reduced to metal. The effect of the added substance varied according to the method of mixing it with the catalyst. In general, an accelerating effect was observed when the added substance was mixed with the nickel compound before reduction, but addition of large amounts of the substances had a prejudicial effect, and sodium carbonate in any proportion acted injuriously. Water, which has a poisonous action upon weak catalysts, they assert has no injurious effect upon a powerful catalyst, such as nickel.

639. Ellis²⁴ prepares a nickel catalyst with an insoluble sulphate as a promoter (accelerator). This is made, for example, by mutual precipitation of barium hydroxide and nickel sulphate, with or without calcium, magnesium, palladium or other compounds.

640. Bosch, Mittasch and Schneider²⁵ suggest a form of catalytic material useful for carrying out hydrogenation and dehydrogenation rapidly, with certainty and at comparatively low temperatures. An intimate mixture of a common metal, iron, nickel, cobalt and copper, with a phosphate of an alkaline earth metal as a promoter, is employed. It is necessary to effect an intimate mixture of the catalytic metal and the promoter. If calcium phosphate be employed as the promoter, the oxide or carbonate of the catalytic metal can be mixed with calcium phosphate and the mixture thereupon be heated and reduced. A still better method consists in taking an insoluble salt, such as the carbonate, or an oxide of the catalytic metal, and adding to it a solution of a calcium salt, for instance, calcium nitrate, and then to add the necessary quantity of phosphoric acid, either as such or in the form of ammonium phosphate, or alkali metal phosphate, in order to convert the calcium into phosphate. It is preferred to employ basic phosphates, such as tri-calcium phosphate, as promoters.

641. It is advantageous for the purpose of making a very active contact mass to prepare the catalytic metal from carbonaceous salts or mixtures of such salts, for instance, from carbonates or from formates. It is often useful to add to the mixture, bodies of inorganic or

²¹ *Seifen. Ztg.*, 1914, 1133; *Zeitsch. angew. Chem., Referat.*, 1915, 220; Ger. Pat. 282,782, December 12, 1913; *Chem. Ztg. Rep.*, 1915, 155. Austrian Pat. 72,758, November 25, 1916. See also U. S. Pat. 1,271,013, July 2, 1918.

²² Brit. Pat. 2,307, Jan. 28, 1914; *Chem. Abs.*, 1916, 125; *J.S.C.I.*, 1915, 970.

²³ Rikwagaku Kenkyujo Iho (*Rep. Inst. Phys. Chem. Research*), 1923, 2, 1; *J.S.C.I.*, 1923 43, 728A.

²⁴ U. S. Pat. 1,426,629, Aug. 22, 1922; *cf. Chem. Abst.*, 1922, 16, 352.

²⁵ U. S. Pat. 1,215,335, February 13, 1917. See also 1,271,013, July 2, 1918.

organic nature, which act either as carriers or as binding agents, or which increase the porosity of the contact mass. Asbestos, charcoal, or pumice may be used. The catalytic metal can be employed either in a state of fine division or in a more compact form, such as wire netting, or wool, or in sheet form. Catalytic mixtures made according to this method can be used for the hydrogenation and dehydrogenation of compounds containing carbon and are of particular value for the hardening of fats and fatty acids. The reaction can be carried out either at ordinary pressure or under increased pressure, for instance, above 50 atmospheres and in most cases proceeds sufficiently rapidly at temperatures below 180° C.

EXAMPLE.—Suspend 5 parts by weight of nickel carbonate in a solution of 1.3 parts of calcium nitrate, and then precipitate the calcium by the addition of 0.7 part of ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). Filter, wash well, dry and reduce with hydrogen at about 350° C. This contact mass may be employed in the reduction of cottonseed oil by means of hydrogen at about 130° C. In another case the same investigators employ an oxide of boron as a promoter, and as an example they recommend to mix freshly precipitated nickel carbonate with 10 per cent of its weight of ammonium borate previously dissolved in water. The product is dried and reduced. Calcium borate may be similarly used. This catalyzer is recommended for hardening fish oil.³⁶

642. Mixed Catalysts Containing Free Carbon. In the preparation of a catalytic body Ellis³⁷ recommends the use of wood charcoal which possesses the property of absorbing or occluding hydrogen and when incorporated with nickel or other metal catalyst serves as an activator and storehouse of hydrogen. If nickel is used, a ratio of 1 part of metal to 4 parts of charcoal is best not exceeded. The metallic compound may be precipitated more or less on the surface of the charcoal particles by wetting the latter with a solution of a precipitant and adding a solution of a nickel salt.

643. An essentially similar catalyst³⁸ has been proposed by Nicodemus, though the method of arriving at the result is different. Carbonizable material with a cellular structure, such as peat or wood, is saturated with catalytic material in solution or in the colloidal form, and, after compression in moulds, is carbonized in the presence of gases containing ammonia, and then calcined.³⁹

644. Ellis⁴⁰ deposits nickel electrolytically in a highly extended form (either independently) or on a carbonaceous body such as finely divided graphite or charcoal.⁴¹ According to another method Ellis⁴² treats purified charcoal with ammoniacal solution of nickel hydroxide so as to give 10–30 per cent of nickel on the weight of charcoal. After drying and elimination of ammonia, the metal is reduced in hydrogen. This procedure is expanded and modified⁴³ by saturating charcoal with a solution of a nickel compound (e.g., acetate, sulphate, or an ammoniacal solution of nickel hydroxide; the nitrate is less suitable). The product is reduced in hydrogen at a low temperature. If the nitrate has been used reduction should be followed by prolonged heating in nitrogen. In a second modification freshly precipitated nickel carbonate is mixed with a binder, such as sugar or dextrin, and the charcoal is coated with this mixture.

645. Ittner⁴⁴ impregnates charcoal with certain mineral substances (e.g., compounds of earth metals or of alkaline earth metals, alumina, silicates of aluminium, calcium, magnesium and cerium), and then with a compound of nickel (or other catalytic metal). On reduction a catalyst of exceptional activity in hydrogenation is said to be obtained.

646. Byers treats sugar with sulphuric acid. The resulting porous sugar charcoal is impregnated with a solution of nickel nitrate. The nitrate is decomposed by treatment with sodium hydrate or with sodium carbonate: the mass is washed and dried. Alternatively the nitrate may be decomposed by heat. In all cases reduction is effected by heating in hydrogen not above 360° C.⁴⁵

³⁶ U. S. Pat. 1,215,334, Feb. 13, 1917.

³⁷ U. S. Pat. 1,060,673, May 6, 1913; cf. U. S. Pat. to Ellis, 1,088,673, Feb. 24, 1914.

³⁸ Ger. Pat. 438,071, June 14, 1924, assigned to I. G. Farbenind. A.-G.

³⁹ Brit. Chem. Abst., 1927, 467B.

⁴⁰ U. S. Pat. 1,151,003, Aug. 24, 1915.

⁴¹ See also: U. S. Pat. 1,300,414, July 4, 1919; *J.S.C.I.*, 1919, 28, 544A.

⁴² U. S. Pat. 1,156,674, Oct. 12, 1915.

⁴³ U. S. Pat. 1,320,039, Oct. 28, 1919; *Chem. Abst.*, 1920, 135.

⁴⁴ U. S. Pat. 1,238,774, Sept. 4, 1917.

⁴⁵ U. S. Pat. 1,470,552, Oct. 9, 1924; *Chem. Abst.*, 1924, 177.

stances including kieselguhr. The latter material is referred to as a catalyst carrier for general use and not particularly for one purpose. Kieselguhr should therefore be regarded as a readily available carrier for nickel from the days when the oil-hardening process was in its infancy.⁵⁰

651. According to Erdmann,⁵¹ priority in the use of kieselguhr as a carrier for a nickel catalyst in oil hardening belongs to Kayser who applied for a patent in the United States on January 10, 1908 (U.S. Pats. 1,004,034, 1911, and 1,008,474, 1911). Erdmann and Bedford⁵² used pumice as a carrier for a nickel catalyst in the hydrogenation of fatty acids and esters.

652. On Aug. 6, 1910, Paal applied for a patent in Germany for the use of palladium on kieselguhr in oil hardening (Ger. Pat. 236,488, July 7, 1911, to the Verein. Chem. Werke, A.-G.).

653. A variety of material has been used for catalyst support. The following list is given by way of exemplification of this diversity and is not exhaustive: Aluminum and other metals, alumina and other metallic oxides, bauxite, alundum, kaolin and other clays, pumice, fuller's earth, kieselguhr, asbestos, talc, mica, barium sulphate, dry magnesium sulphate, glass, ceramic surfaces, silica in various forms, fibrox (fibrous oxy-carbide of silicon), carborundum, charcoal in various forms, graphite. Some of these materials, in addition to their function as supports, have, in certain catalyses, a distinct promoter action. Others, such as kieselguhr and fuller's earth, are useful in clarifying the product. Indeed this seems very early to have prompted their use in the hydrogenation of oils. The product of hydrogenation by unsupported nickel contained the catalyst in such fine suspension as to hinder filtration: but when nickel supported on kieselguhr was used, though the catalyst did not settle out completely, the oil was easily clarified by filtration through its own nickel-kieselguhr sludge.

654. Yet another important property of carriers is brought out in the following table:

Figures Showing Correlation between Specific Gravity, Apparent Volume and Catalytic Activity of Unsupported and of Supported Nickel.⁵³

Source of Reduced Nickel	Temperature of Reduction	Reduced Nickel		Catalytic Activity
		Density	Appt. Vol. Cc. per Gram	
Powdered fused oxide.	500° C.	8.14	0.52	None.
Precipitated hydroxide.	300° C.	7.85	0.83	Fair.
	500° C.	8.18	0.56	Very little.
Precipitated on Kieselguhr. . .	500° C.	1.85	2.67	Very active.

⁵⁰ *Seifen. Ztg.*, 1915, 310.

⁵¹ *Seifen Ztg.*, 1915, 239.

⁵² *Ber.*, 1909, 1324.

⁵³ Armstrong and Hilditch. Catalysis at solid surfaces. *Inst. internat. de chimie Solvay*, 1925.

647. Metallized Carbon Catalyst.⁴⁶ Carbon on and in which catalytic metal is deposited is said to be an efficacious catalyst in the reduction of the hydroxy and acid compounds in tars from carbonization of coal, etc. For example, paracresol is reduced to toluene by distilling it mixed with hydrogen, over metallized carbon maintained at 430° C.

648. Experiments with a Growth-Impregnated Charcoal Catalyst. Twigs of willow were grown in nickel nitrate and ammonium nitrate solutions (50 g. per liter). After carbonization and powdering, the charcoal was reduced at red heat with ammonia gas. Commercial linseed oil was hydrogenated at 1 atmosphere pressure at temperatures of 150°, 160°, 170° and 180°. The charcoal powder contained 30 per cent of nickel and was used at the rate of 1 g. per 100 cc. oil. The iodine number was reduced from 183 to 166 in 70 minutes at 150°, to 128 in 70 minutes at 160°, to 107 in 70 minutes at 170°, and to 104 in 70 minutes at 180°. The efficiency of the charcoal appeared to be well maintained and removal of the charcoal from the oil presented no difficulty if the filtration was carried out while hot.⁴⁷

CARRIERS

649. Carriers,⁴⁸ or inert supports for solid contact catalysts are frequently used. Contact catalysis having been soon recognized as a surface phenomenon, what was more natural than to seek to increase the surface presented by the catalyst to the reactants? Thus we have platinum-black and platinum sponge used. To-day the idea that a solid catalyst should be finely divided is so commonplace that it seems almost an original intuition of the human mind. The early contact catalysts were expensive, so greater surface was secured by spreading them in tenuous layers on such substances as asbestos. The same procedure is used to-day with platinum, palladium and other costly metals, though in some important processes metallic gauzes are used.

649A. An interesting inert support for the catalyst is used in the Schroder-Grillo contact process of sulphuric acid manufacture. Crystalline magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) is treated with a solution of a platinum salt and heated in presence of sulphur dioxide. The platinum is reduced and the sulphate is dehydrated and in this process the latter swells up very much. The platinum on the surface of the dry sulphate amounts to about 0.25 per cent of the weight of the latter. With 5 g. of platinum 1 ton of "oleum" can be produced with a loss of only 20 mg. of metal.⁴⁹

650. The precipitation of catalytic substances on carriers has been known for about fifty years, dating from the German Patent No. 4566 by Clemens Winkler in Freiberg, who stated that he could use "as indifferent supports or carriers of the true contact agent almost all fluffy, porous substances, especially asbestos but also glass, slagwool, pumice stone, kieselguhr and clay and, provided the use of the material does not require high temperatures, also organic fibrous material such as cellulose, cotton, guncotton and sponges. Winkler describes thoroughly how the catalytic metal is precipitated upon these various sub-

⁴⁶ Brit. Pat. 225,885, Dec. 8, 1924, to Naaml. Vennoots. Handelsonderneming Feynald Maatschappij tot Exploit. van Octrooien, assignees of Stadnikoff. The description does not expressly exclude non-catalytic reactions.

⁴⁷ Pickles, *Chem. Age* (London), 1923, 8, 166; *Chem. Abst.*, 1923, 17, 1899.

⁴⁸ Although the word substrate has long been firmly established as a term for the substance acted on in fermentation and is, therefore, justifiably applied to the substance acted on in catalysis, it has, unfortunately, been recently applied in patents to the carrier of a catalyst. This is a case of conflict between etymology and established usage.

⁴⁹ *J. Soc. Chem. Ind.*, 1903, 22, 348; Rideal and Taylor, *loc. cit.*, p. 86.

The point brought out by this table which is of present interest is that, by supporting nickel upon kieselguhr, a higher temperature can be used in the reduction, without impairment of the catalytic activity. It is also stated that nickel catalyst so supported is less sensitive to poisons.

655. Effect of Supports. Pease and Stewart ⁵⁴ have compared the catalytic activity and the adsorptive power of iron, cobalt, nickel, copper and silver. The metals deposited on diatomite brick were used as catalysts in the hydrogenation of ethylene. The catalysts were similarly prepared and are therefore comparable. Cobalt and nickel caused instantaneous action at $-20^{\circ}\text{C}.$; iron was moderately active at 0° , copper at $50^{\circ}\text{C}.$, and silver at $100^{\circ}\text{C}.$ A support gives stability where it is needed, but it yields a catalyst of somewhat smaller surface. Supported copper is a poorer catalyst than the unsupported material. This metal can be reduced at comparatively low temperatures, and the use of a support, which obviates reduction at high temperatures and the accompanying sintering and deactivation, is of no particular advantage as it is in the case of the other metals. More hydrogen is adsorbed by nickel and cobalt than by the other metals, and more ethylene by iron. In the presence of silver at $100^{\circ}\text{C}.$ the reaction rate is proportional to the hydrogen, and independent of the ethylene concentration. In the presence of iron at 0° excess of hydrogen increases the rate, while excess of ethylene has little influence. Heats of activation are recorded. The highly active hydrogenation catalysts are those metals which in ionization produce large numbers of stable complexes in solution. This is probably due to a capacity for electron sharing, and it may be that this associative property of the metal brings the reactants together and renders them both labile, so that a system of lower free energy is produced.⁵⁵

656. Adsorptive Power of Carrier and Catalytic Activity. An important paper has been published by Sabalitschka and Moses ⁵⁶ in which are collated the adsorptive powers of certain carriers and the activity of the metal-support catalyst. The catalytic hydrogenation of maleic and fumaric acids and sodium cinnamate were examined in the presence of palladium deposited on blood, beech, fungus, bone, and sugar charcoal and on barium sulphate and kieselguhr. The adsorptive power of the catalysts towards hydrogen could not be definitely determined. The sequence of diminishing powers towards fumaric and maleic acids and sodium cinnamate was: blood, beech, fungus, bone, and sugar charcoals; barium sulphate and kieselguhr (equal). The activity of the catalysts obtained by loading different carriers with an equal amount of palladium depended to a greater or less extent on the carrier. With freshly prepared materials, the activity towards all three unsaturated substances diminished in the sequence: blood, fungus, beech, bone, and sugar charcoals; barium sulphate and kieselguhr; palladium without carrier. The activity was also dependent on the manner in which any given carrier was charged with a definite amount of metal; for example, sugar charcoal, barium sulphate, and kieselguhr catalysts,

⁵⁴ *J. Amer. Chem. Soc.*, 1927, **49**, 2783.

⁵⁵ *Brit. Chem. Abst.*, 1928, 29A.

⁵⁶ *Ber.*, 1927, **60B**, 786.

prepared from the hydroxide and subsequently preserved, had a greater activity than fresh catalysts prepared from the chloride. Ignition in a high vacuum and saturation with hydrogen diminished the activity of all catalysts to an extent which increased with the number of such treatments; the catalyst was not reactivated by oxygen. The adsorptive power of the catalysts towards hydrogen depended on the type of carrier and was scarcely affected by the mode of charging with palladium; palladium-free carriers did not absorb hydrogen measurably.

656A. The activity of the palladized carriers depended greatly on the extent to which the palladium compound was adsorbed by the carrier previous to reduction. With carriers of low adsorptive power, more efficient catalysts were obtained by use of the readily adsorbable palladium hydroxide in place of the chloride, whereas with good adsorbents little difference was observed in the various products. The activity of palladized barium sulphate was dependent on the degree of division of the palladium. The catalytic activity was influenced in varying degree by the volume of the liquid in which it was distributed during hydrogenation.

Separate determinations of the adsorptive powers of palladized catalysts toward hydrogen and the substances undergoing hydrogenation and of the catalytic activity of these catalysts under similar conditions indicated a proportionality between the three properties, but show that the catalytic activity did not depend directly on the magnitude of the adsorption. Sabalitschka and Moses arrive at the conclusion that the important function of the carrier is the provision of a *larger* surface (contrast para. 655) and favorable disposition of the catalyzing metal by adsorption of the compound from which it is formed by reduction; it also secures a better distribution of the metal in the reaction mixture and preserves the fine division of the metal by hindering aggregation, which otherwise takes place readily.⁵⁷

657. According to Crosfield⁵⁸ kieselguhr or the like is impregnated with a solution of nickel sulphate and the impregnated material treated with alkali hydrate to precipitate nickel hydrate in and on the porous material. The product is then well washed, dried and reduced. If kieselguhr is used the powder should contain about 30 per cent of metallic nickel.⁵⁹

658. A similar procedure is recommended by Kayser.⁶⁰ In this case, however, the nickel sulphate or other nickel salt in concentrated solution may be used in an amount to saturate kieselguhr while leaving it in an apparently dry condition, when it is incorporated with a molecular proportion of powdered carbonate of soda and the mixture thrown into boiling water, dried and reduced.

659. Kayser states that there are various known ways for producing metallic powders in a state of fine division. Nickel powder, which for many purposes is recognized as the most potent catalyzer technically available, is, for example, most conveniently produced by acting upon such nickel compounds as the chloride, oxide, hydrate or carbonate at an adequate

⁵⁷ Ber., 1926, 60B, 786; Brit. Chem. Abst., 1927, 427A.

⁵⁸ Brit. Pat. 30,282, 1910.

⁵⁹ Ubbelodhe and Woronin (*Petroleum*, 1911, 7, 9) prepared a catalyzer by crushing a plate of porous clay (which had been ignited) to form particles of about the size of peas. Nickel nitrate was melted and heated until water vapor ceased to be evolved. Then the clay particles were added and the mass was stirred and strongly heated to expel the oxides of nitrogen. This step was followed by reduction with hydrogen at 360° C.

⁶⁰ U. S. Pat. 1,143,343, June 15, 1915.

temperature with hydrogen. The catalytic energy of such a powder, however carefully prepared, he says, is at best an uncertain quantity; frequently it is feeble, and sometimes, for no conclusive reason, it is altogether lacking. Furthermore, powder thus produced is specifically heavy and he claims cannot be easily kept in suspension in a liquid medium like oil, when that is desired, nor can it, since it forms an almost impervious sediment, be readily separated and recovered from such liquid medium by a contrivance like the filter press. The same objections, he says, apply to nickel powder prepared by other means; and, in the endeavor to improve on these, Kayser brings a compound of nickel, such as the nitrate, oxide, hydrate or carbonate, into intimate contact with an inert, absorptive and comparatively bulky mineral substance, such as kieselguhr and infusorial earth, dries and comminutes the product, and reduces the powder thus produced. In one case he saturates kieselguhr with a solution of nickel nitrate, dries the mixture, employing in the case of the nitrate sufficient heat to expel the nitric acid, grinds the resulting product and reduces with hydrogen. Another way is to permeate or saturate kieselguhr with a solution of nickel chloride, nickel sulphate or other soluble nickel salt, enter the resulting product, with or without previous drying, into a boiling solution of carbonate or hydrate of soda or other suitable precipitant, remove the soluble salts formed by washing, dry and comminute the residue, and reduce it as before. A third and preferred method, as stated, is to saturate the kieselguhr with a solution of nickel chloride, nickel sulphate or other nickel salt, using so much solution only as will leave the kieselguhr in an apparently dry and freely workable condition, incorporate a molecular proportion of powdered carbonate of soda or other powdered precipitant, throw the mixture with constant stirring into boiling water, remove the soluble salts formed by washing, dry and comminute the mixture, and reduce as before. To develop the highest catalytic efficiency, Kayser states that the kieselguhr should become evenly and completely coated and permeated, plated as it were with a film of metal, and that a catalyzer composed of 1 to 2 parts by weight of metallic nickel and 4 parts by weight of kieselguhr has however proved very effective in saturating fats and oils by means of hydrogen. The author can see no advantage in permeating or impregnating the interior canals of the carrier with catalytic metal when the catalyst is to be used for hydrogenating fatty oils.⁶⁶⁰ The porous support used by Sabatier and Senderens, to be sure, was impregnated with reduced nickel, but these investigators directed their attention to the hydrogenation of readily volatile substances, capable of diffusing into the interior of the nickel-laden porous material.

660. In another U. S. Patent (1,008,474, of Nov. 14, 1911), Kayser further sets forth the use of an inert pulverulent material such as kieselguhr as a carrier for the nickel catalyzer and he claims the process of hydrogenating oil involving agitation of a metal-impregnated inert pulverulent carrier (kieselguhr) with a fatty oil in the presence of hydrogen.

661. Wesson⁶¹ prepares a catalyzer by first dissolving nickel nitrate in water and then adding ammonium hydrate, which causes nickel hydrate to be precipitated in the form of a voluminous, flocculent precipitate. Care should be taken to add only a sufficient quantity of ammonium hydrate to form the precipitate, as an excess will break down the hydrate of nickel and cause it to redissolve. In thus using ammonia as a precipitant, sulphates or chlorides which may be present in the nickel nitrate will be converted into sulphates or chlorides of ammonium and these are volatilized at the temperature at which the nickel is subsequently reduced. This serves as a method of purification, which is very desirable in order to produce an active catalyzer. After the precipitate of hydrate of nickel is formed, the supernatant liquid containing ammonium nitrate and some unprecipitated nickel salts may be decanted off, leaving nickel hydrate and water with a small amount of ammonium salts dissolved in the water. *This flocculent precipitate is then mixed with the inert carrier to which it is to be applied, as, for instance, asbestos.* The precipitate and the support are then dried to expel the water and are heated at a temperature of say 500° C. in a current of hydrogen until the nickel has been reduced to a finely divided condition, covering the asbestos fibers or other support used. The ammonium nitrate that remained in the water assists in this. As the support covered by the flocculent precipitate is heated, the ammonium nitrate is decomposed, leaving most of the nickel hydrate around it in a very fine and spongy condition, in which form it is more easily reduced by the hydrogen, and at the same time the operation puts it in such shape as to present a greater surface for contact action. There are stated to be substantial advantages in applying the flocculent hydrate of nickel to the sup-

⁶⁶⁰ Note para. 941.

⁶¹ U. S. Pat. 1,143,339, June 15, 1915.

port, instead of applying to the support a solution of a salt and afterward adding a precipitant. For in the former case the hydrate acts only on the surface of the support (which is the place where it is wanted) and is not soaked up into the internal pores of the support, as it would be if the support were treated with a solution of a salt and precipitation were brought about afterward.

662. Nickel hydrate such as used in the foregoing (Wesson) catalyzer is prepared according to Woodruff⁶² in the following manner: nitrate of nickel or other nickel oxygen salt is dissolved in sufficient water to form a dilute solution, which should contain about 1 per cent of the crystalline salt, and the solution is then brought to a temperature in the neighborhood of the boiling-point. Satisfactory results are obtained at a temperature of approximately 95° C. Sufficient hydroxide of ammonium to theoretically precipitate all the nickel present is then added. In practice an ammonium hydroxide solution of a specific gravity of about 26° Baumé is used. The correct amount of a given solution of the ammonium hydroxide to add to the solution of the nickel salt may be determined by slowly adding the ammonia to a small quantity of the nickel solution under the above conditions, and noting the point at which the precipitate commences to dissolve. A slightly smaller proportion of ammonia should then be added to the bulk of the nickel solution. Under these conditions it will be found that practically all the nickel will be precipitated in the form of flocculent nickel hydroxide. If a more concentrated nickel solution be employed or if precipitation be brought about at a lower temperature or if an excess of ammonia be added, the amount of nickel thrown down will be relatively decreased. After the nickel hydroxide is precipitated it may be applied to a support while still in the solution in which it was formed, or the supernatant liquid may be decanted off. By the use of a very dilute solution of the nickel salt from which the precipitate is formed, practically all of the impurities are said to be removed, when the supernatant liquid is decanted off, whether before or after the application of the precipitate to the support, thus eliminating the necessity of washing the catalyzer. The precipitate and the support are then dried to expel water and are heated to a temperature of about 500° C. in a current of hydrogen.

663. Snelling⁶³ observes that in the use of a siliceous carrier with an oxide it is difficult to prevent more or less formation of slaggy compounds, but that a catalyzer of high reactivity can be prepared by heating the metallic formates, the reduction of which takes place at a very low temperature, and proceeds smoothly.

Nickel, cobalt, iron and copper formate, etc., may be used; and these salts may be employed in the dry state where a powder is required; or a porous carrier may be soaked with a solution of the formate, dried and reduced. On heating, the formates decompose with an evolution of carbon monoxide and hydrogen, both strongly reducing gases; and this evolution of these gases in *statu nascendi*, allows the formation of highly reactive metal at very low temperatures. It is not necessary as in the case of nitrates to supply the reducing means from another source; which is regarded by Snelling as an advantage in the case of forming the catalyst on a support. In the formates, the combustible and the oxygen of the metal oxide are in atomic or molecular contact; a contact differing from that of the oxide as powder in an atmosphere of hydrogen. And, as the reduction of the metal oxide and the oxidation of the combustible as a total reaction is exothermic, a reduction change started in one portion of a mass of formate tends to spread through it; the reaction it is stated can be initiated at one point and allowed to spread through the material as a self-propagating reaction. The reduction may be effected at a comparatively very low temperature; a temperature at which there is no tendency of the reduced metal to sinter or of the oxides to slag.

664. In making reactive copper where the metal is desired in pulverulent form, copper formate is first dried at a low temperature and is then cautiously heated in a container to the lowest temperature at which the formation of metal becomes evident. The air in the tube is best displaced by hydrogen prior to heating. The formate may be dried in the container in which reduction is subsequently to be effected. In so doing it is advantageous to pass through a stream of hydrogen or other non-oxidizing gas. This stream carries away as fast as formed the water produced in drying and that produced in the subsequent reduction

⁶² U. S. Pat. 1,143,343, June 15, 1915.

⁶³ U. S. Pat. 1,122,811, December 29, 1914; *J.S.C.I.*, 1915, 182.

and much facilitates both operations. A vacuum may be used in lieu of hydrogen. Where the copper is carried on a support, the carrier may be soaked in a solution of copper formate and the impregnated material dried and heated in the same way. It is particularly advantageous in this case after placing the impregnated carrier in the reduction vessel to produce a vacuum to remove adsorbed air. Hydrogen is then allowed to enter and the material heated.

665. The porous carrier employed may be any of the usual refractory materials. For nickel, cobalt, iron, copper, etc., where used for hydrogen addition, as in hardening fats, the carrier may be coke. Where used in oxidizing reactions, as in the manufacture of formaldehyde, the carrier is better an inoxidizable material, such as pumice-stone, baked clay, kieselguhr, etc. For many purposes Snelling finds that alundum is a desirable carrier since in some reactions alumina has a catalytic action. It is particularly advantageous in making a copper catalyst for the manufacture of formaldehyde. For many purposes in catalytic operations Snelling states it is desirable to have a column of catalytic material wherein the carrier has different proportions of catalyst at different points throughout the column. For example, in making formaldehyde from methyl alcohol and air it is advantageous to have the mixed vapor and air pass through an alundum carrier containing a relatively small amount of copper, then past a carrier containing more, and so on until the mixture finally passes a carrier relatively rich in catalyst. It is regarded as advantageous to have the concentration of the reactive bodies inversely proportional in any given zone of catalysis. Similarly in hydrogenation processes involving the addition of hydrogen to vapors and gases, it is advantageous to have the gas mixture first pass through a carrier containing relatively little reduced nickel and subsequently past a carrier containing more nickel.

666. As stated, the reduction of the formate should be at the lowest possible temperature; and the material should be brought to this temperature rather gradually. Careful observation of any given formate will show to the eye the point where reduction begins. Any violent heating causes a sudden decomposition of the formate with the liberation of carbon monoxide and hydrogen in the gaseous form; after which reduction can only be in the ordinary way; viz., by a reducing atmosphere. With violent heating the reaction, under the catalytic influence of the metal, is apt to be irregular and result in the production of carbon and other bodies.

667. Silica Gels and the Like. The great surface per unit mass afforded by such substances as silica gel (*cf.* para. 202) makes them promising materials for catalyst supports. A number of such supported catalysts are available. The carriers are of various kinds, e.g., Patrick's silica gel, "monox," the silica obtained by treating the tetrafluoride with water, alumina, stannic oxide and tungstic oxide. Three leading methods are employed in the preparation of the catalyst. In the first metals are reduced from their solutions by hydrogen adsorbed by the gel (para. 668). In the second the hydrogel is treated a solution of a metal salt reducible by heat, the gel is then dried and heated (para. 672). In the third method the material is impregnated with a metal compound and, after drying, the metal is reduced in hydrogen as usual (para. 673).

668. Reducing Action of Hydrogen Adsorbed in Silica Gel. Latshaw and Reyerson⁶⁴ report that solutions of copper, silver, gold, platinum, palladium are reduced, with the formation of a fine metallic deposit, on silica gel saturated with hydrogen. Nickel is not so reduced. The metallized gel is catalytically active. The details of the method as given by Reyerson⁶⁵ are as follows:

Adsorbed gases having been removed from the silica gel by exhaustion in a vacuum, hydrogen is admitted and the temperature is lowered to -15° to -30° . When adsorption of the hydrogen is complete the gel is treated with a solution of a metal salt, such as a salt of

⁶⁴ *J. Am. Chem. Soc.*, 1925, 47, 610.

⁶⁵ U. S. Pat. 1,547,236, July 28, 1925. This is distinguishable from Brit. Pat. 286,309 March 3, 1927, to Latshaw and Judefind (assigned to Silica Gel Corp.) apparently only by the fact that the latter patent covers charging the gel with any reducing gas (sulphur dioxide, carbon monoxide, hydrogen sulphide), hydrogen being mentioned only incidentally.

copper, silver or platinum. In time the surface of the gel becomes covered with a metal film of ultramicroscopic fineness.

669. Adsorption of Gases by Metallized Gels. The metallized silica gels prepared by the method just described have been used by Reyerson and his associates in a number of researches. The adsorption of gases by these gels was studied by Reyerson and Swearingen.⁶⁶ The adsorptions were measured at 0°, 64–65°, 100°, 138°, and 218°. Hydrogen is appreciably adsorbed by the copper, platinum, and palladium gels, carbon monoxide by all the gels except that of copper, while ethylene is absorbed more strongly than by silica gel alone. Oxygen is specifically absorbed by all the gels, especially by the copperized gel. Methane shows no specific effect, neither does carbon monoxide, except possibly in the case of copper. Rise of temperature rapidly reduces adsorption. Successive metallizations of the gel by platinum have no great effect except in the case of carbon monoxide, where a steady increase in the amount adsorbed occurs up to four metallizations. With silica gel alone, the amounts of the above-mentioned gases adsorbed at 0° and 760 mm. increase with the boiling-point of the gas, except in the case of carbon monoxide. For all gels, metallized or not, the Freundlich equation holds whenever considerable adsorption takes place.

670. Hydrogenation of Ethylene. The catalytic hydrogenation of ethylene by metallized silica gels has been studied; platinized, palladized and copperized gels being used. The mixture of ethylene and hydrogen was passed over the catalyst maintained at the desired temperature and the extent of hydrogenation was determined by analyses of the product for ethylene. The effect of temperature and of the rate of flow and the composition of the gas mixture upon hydrogenation was determined for three catalysts. For a standard rate of flow of mixtures with 25 per cent ethylene, over the range 0° to 240° C. the palladized and platinized gels reached their maximum efficiency at 60° C. (99.7 per cent and 98.8 per cent respectively), while the copperized gel, over the range – 20° to 360° C. was most efficient at 240° C. (59.9 per cent). The temperature-efficiency curve is normal for the first two metals, but irregular for copper, there being a minimum at 30° C. This is attributed to the formation of an inactive copper hydride, most stable at room temperature. A fall of efficiency was observed with increased gas velocity for all three catalysts, the effect being most marked with the copperized gel. It is suggested that this is due to the comparative scarcity of active areas in the copper catalyst in which the metal atoms are not in the crystal lattice of the metal. Experiments with gaseous mixture of various compositions were carried out at 27° and 170° C., and indicated that the efficiency of all three catalysts was inversely proportional to the partial pressure of the ethylene.⁶⁷

671. Hydrogenation of Acetylene.⁶⁸ The hydrogenation of acetylene using silica gels metallized with platinum, palladium, and copper has been studied by

⁶⁶ *J. Phys. Chem.*, 1927, **31**, 88; *Brit. Chem. Abst.*, 1927, 198A.

⁶⁷ Morris and Reyerson, *J. Phys. Chem.*, 1927, **31**, 1220; *J. Inst. Petr. Tech.*, 1927, **221A**; *Univ. Oil Prod. Co., Libr. Bull.*, Feb. 18, 1928.

⁶⁸ Morris and Reyerson, *J. Phys. Chem.*, 1927, **31**, 1332; cf. Swearingen and Reyerson, *Ibid.*, 1928, **32**, 113; U. S. Pat. 1,547,236.

the method employed in the case of ethylene. Ethylene and ethane are both produced, the palladium-silica gel becoming active at 50°, the platinum gel at 100°, and the copper gel at 200°. Palladium is the better catalyst for the production of ethylene, regardless of the original mixtures used, while platinum favors the production of ethane. Further, as the ratio of acetylene to hydrogen increases from 1:10 to 3:1, the production of ethylene passes through a maximum. It is probable that the combined adsorption of gel and metal produce a more satisfactory condition for the catalysis of ethylene formation than does the adsorption of either alone.⁶⁹

672. Heat Reduction of Metals on Gels. The second method of producing metallized gel is described by Miller and Connolly.⁷⁰ They prepare catalysts by treating a hydrogel with a solution of a metal compound which yields a catalyst on heating. The gel is then dried and heated. The gel may be alumina, silica, stannic oxide, tungstic oxide, etc.

673. Hydrogen Reduction of Metal on Gel. A form of nickel catalyzer was prepared in the author's laboratory by decomposing silicon tetrafluoride with water which yielded a very voluminous form of silica.

This material was carefully washed free from chlorides and sulphates and dried. An amount of nickel nitrate crystals equal in weight to the silica was dissolved in 5 parts of water and the solution was thoroughly mixed with the silica. The mixture was dried and ignited until all fumes of nitrogen oxides were expelled. The dark powdery material was heated in a current of hydrogen for one hour at 327° C., cooled and preserved under oil to prevent oxidation. This material carried approximately one-sixth of its weight of nickel. To a quantity of cottonseed oil, an amount of this catalyzer was added to introduce 0.7 per cent of nickel and hydrogen was passed through the oil and catalyzer for two and one-half hours at 175° C. At the end of this time the hardened fat produced was found to have an iodine number of 29.8.

674. Silicious material, known as monox or silicon monoxide, which is of a very light and voluminous character and is prepared in an electric furnace, was tested in the author's laboratory as a supporting material for nickel in the preparation of a catalyzer. By means of a solution of nickel nitrate the monox was saturated with the nickel solution and the mixture ignited until red fumes ceased to be evolved. The product was then reduced to a fine powder and heated for one hour in a current of hydrogen at a temperature of 340° C. The reduced catalyzer was preserved under oil. The proportions used in preparing the materials were 10 parts by weight of nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to 8 parts of monox. Cottonseed oil containing 5 per cent of this catalyzer or approximately 1 per cent of the reduced nickel was heated for three and one-half hours to 174°–180° C., while a continuous stream of hydrogen was passed through the oil and the melting-point of the hardened product which resulted was 48.2° C.

675. It has also been proposed to employ a finely crystalline nickel compound, such as the nitrate, which is mixed with silicic acid or other carrier and reduced for the production of a highly active catalyst.⁷¹

676. In another procedure an irreversible colloid, e.g., silica, alumina, iron

⁶⁹ *Brit. Chem. Abst.*, 1927, 1038A.

⁷⁰ *Brit. Pat.* 280,939, Nov. 19, 1926 (to Silica Gel Corp., assignees); *Chem. Age* (London), 1928, 18, 85; cf. *U. S. Pat.* 1,695,740, Dec. 18, 1928, to Patrick (assigned to Silica Gel Corp.). *U. S. Pats.* 1,696,644 and 1,696,645, both of Dec. 25, 1928, to Patrick (assignee to Silica Gel Corp.) describe a copper-silica-gel catalyst and a nickel- or cobalt-silica-gel catalyst respectively.

⁷¹ *U. S. Pat.* 1,696,666, Dec. 16, 1928, to Schirmacher, Stolz, Schlichenmaier and Krohs (assigned to I. G. Farbenind. A.-G.). *Brit. Pat.* 255,884.

oxide, is prepared as a sol or jelly, and, before being dried, is mixed intimately by mechanical means with one or more catalytic substances in the liquid or finely divided solid state. When the colloid is a sol the mixture is allowed to set to a jelly, dried, and purified by washing before or after complete drying.⁷²

677. Silicic acid. Another type of silica carrier is made by Gover's process.⁷³ A gel of colloidal silicic acid is dried until it becomes irreversible. Impurities are then washed out of the material, which is again dried. This furnishes a product adapted for use as an adsorbent or as a catalyst, or as a catalyst support.

678. Hydrated calcium metasilicate, obtained by treating diatomaceous earth or similar material with lime (magnesia, strontia or baryta) and water, with or without heat, is voluminous and almost gelatinous, one of the uses for it is as a carrier for nickel or other catalysts.⁷⁴

679. "Ageing" of Silica Gel Prevented. To prevent silica gel (10-30 per cent water) from "ageing" by contraction of the solid particles in the presence of a mobile aqueous phase, its water-content is replaced by turpentine or paraffin oil (boiling-point about 200°). The gel may either be immersed in the oil, or soaked with 3-10 per cent of oil and heated to drive off the water vapor, or treated with oil vapor. In order to accelerate the replacement, about 1 per cent of an emulsifying agent, such as clean wool grease or soap, is added to the oil. The gel is subsequently heated to carbonize the oil in its pores. If metallic soaps are used, the resulting gel has marked catalytic properties for certain reactions.⁷⁵

680. Gelatinous Metallic Hydroxides. For the preparation of these a concentrated solution of a soluble salt of a metal the hydroxide of which is insoluble in water, is thoroughly mixed and stirred with a soluble alkali solution of such concentration and quantity that the mixture is faintly alkaline, the mixture being maintained at a temperature below 10°. The gelatinous precipitate is then washed and dried.⁷⁶

681. Preparation of Catalysts from Alloys. Finely divided metals in a highly active form are produced from alloys of the metals with other metals which are decomposed previous to or during their use as catalysts. For example, if nickel-magnesium alloy is applied to moist pumice stone, the magnesium is converted into magnesium oxide or hydroxide, and nickel is deposited in a highly active form. Catalytic material may be prepared in a similar manner from copper-magnesium, copper-calcium, platinum-sodium, copper-aluminium-zinc, and chromium-magnesium alloys. Alloys may also be used in which one of the metals readily absorbs hydrogen, e.g., nickel-lead alloys, or amalgams may be used which are decomposed by heat. Acetone is reduced to isopropyl alcohol at 90°-100° by treatment with hydrogen in the presence of catalytic material prepared by applying powdered copper-magnesium alloy to pumice, spraying with sodium silicate solution, and heating to 300° for forty-eight hours in a cur-

⁷² *Suppl. J.S.C.I.*, Sept. 2, 1927, 653; Brit. Pat. 255,904, July 26, 1926, to I. G. Farbenind. A.-G.

⁷³ U. S. Pat. 1,504,549, Aug. 12, 1924; *Chem. Abst.*, 1924, 18, 3250.

⁷⁴ Brit. Pat. 268,011, Dec. 18, 1925, to Celite Co.

⁷⁵ Brit. Pat. 222,279, Aug. 17, 1923, to Fitzpatrick.

⁷⁶ U. S. Pat. 1,520,305, Dec. 23, 1924, to Patrick (assignor to the Silica Gel Corp.).

rent of hydrogen. Catalysts can be made which are suitable for the conversion of borneol into camphor, carbon monoxide into methyl alcohol, and phenol into cyclohexanol.⁷⁷

681A. An alloy of one or more metals oxidizable by heating in air, with one or more metals oxidized under the same conditions much more easily, yields, when heated, a porous mass, which is of increased catalytic activity. The less oxidizable metal may be copper, aluminum, or nickel, and the more oxidizable metal may be magnesium, calcium, or zinc. A catalyst is made by heating the alloy in air to a temperature at which the greater part of the metals are converted into oxides.^{77a}

682. Effect of Colloid Mill on Supported Nickel Catalyst. A nickel catalyst on kieselguhr was sent several times through a colloid mill. Great reduction of particle size was obtained but the change was accompanied by a fall in catalytic activity. If comminution of the support is desirable this should precede precipitation of the metal.⁷⁸

683. Metallizing Organic Substances.⁷⁹ Fibres and other organic tissues may be coated with metal by exposure to cathode rays *in vacuo*, the cathode being of the metal to be deposited.

MISCELLANEOUS REFERENCES TO CARRIERS

684. Boswell and Dilworth. Mechanism of catalysis by alumina. *J. Phys. Chem.*, 1925, **29**, 1489; *C. A.*, 1926, **20**, 691.

685. Mautner. Silicic acid gel as an adsorbent. *Kolloid-Z.*, 1927, **42**, 273; *Brit. Chem. Abst.*, 1927, 687B. A general article.

686. Vallery. Stability of catalytic palladinized asbestos. *Compt. rend.*, 1927, **185**, 538. Refers only to the use of the catalyst in gas analysis.

⁷⁷ Ger. Pat. 408,811, Apr. 4, 1923, to Schmidt, Bertsch and Ufer (assignors to the Badische Co.).

^{77a} Brit. Pat. 309,743, Apr. 20, 1928, to Howards and Sons, Ltd., Blagden, and Clark; *Chem. Age* (London), 1929, **20**, 478.

⁷⁸ Mashkilleison. *Oil and Fat Industry* (Russia), 1928, No. 1, 24.

⁷⁹ Brit. Pat. 252,710, May 27, 1925, to von Bosse and others.

CHAPTER VII

EXPERIMENTAL APPARATUS

GAS PHASE

700. The first catalytic hydrogenation of an organic compound was the formation of methylamine by passing the vapors of hydrocyanic acid with hydrogen over platinum-black (Debus. *Ann.*, 1863, **128**, 200). Some years later Saytzeff hydrogenated nitrobenzene, in the vapor phase, over palladium-black.¹ In 1897 began the classical researches of Sabatier with Senderens, Mailhe and others.² This work was based, essentially, on the discovery of the remarkable activity of nickel as a hydrogenation catalyst. The process of hydrogenation by passing the vapor of an unsaturated substance with hydrogen over nickel is known as the method of Sabatier and Senderens. The result of all this work was to show that almost any vaporizable, organic compound, unsaturated or capable of reduction, could be catalytically hydrogenated, in the vapor phase, given appropriate temperature conditions and a suitable catalyst.

APPARATUS

701. The apparatus used by Sabatier and his collaborators for hydrogenation in the gas phase is illustrated diagrammatically in Fig. 4.

702. A detailed description of this apparatus and of the method of using it is given in Sabatier's book on catalysis in organic chemistry,³ paragraphs 345 to 357.

703. Reaction Tube. The reaction tube containing the catalyst is 65 to 100 cm. long and 14 to 18 mm. internal diameter. The tube may be laid in a trough on magnesia, but, preferably, is placed in an air-bath. In special cases, for the air-bath an oil or water-bath may be substituted. In still more special

¹ Kolbe, *J. prakt. Chem.*, 1871 [2], **4**, 418.

² Sabatier and Senderens published the results of their earlier work in *Compt. rend.*, **132**, 210, 566 and 1254. A very complete description of their investigations appears in *Ann. Chim. et de Phys.*, 1905 (8), **4**, 319-488. See also Mailhe *Chem. Ztg.*, **1907** (31), 1083, 1096, 1117, 1146 and 1158; *Chem. Ztg.*, **1908** (32), 229 and 244; Willstätter and Mayer, *Ber.*, **1908** (41), 2199; Paal and Amberger, *Ber.*, **1908** (38), 1406 and 2414; Paal and Gerum, *Ber.*, **1907** (40), 2209; **1908** (41), 813 and 2273; **1909** (42), 1553; Paal and Hartmann, *Ber.*, **1909** (42), 2239; Paal and Roth, *Ber.*, **1908** (41), 2282; **1909** (42), 1541; Ipatiev, *Ber.*, **1902** (35), 1047; **1904** (37), 2961; *Chem. Centralbl.*, **1906**, II, 86; *Ber.*, **1907** (40), 1270 and 1286; **1908** (41), 991; **1909** (42), 2089, 2092 and 2100; Ipatiev, Jakovlev and Raktin, *Ber.*, **1908** (41), 996; Ipatiev and Philipov, *Ber.*, **1908** (41), 1001; Padoa and Carughi, *Chem. Centralbl.*, **1906**, II, 1011.

³ Sabatier (tr. Reid). *Catalysis in Organic Chemistry*. Van Nostrand, 1922.

instances, for the hydrogenation of delicate substances, e.g., the benzoic esters, a massive bronze block was employed, the thermometer being placed in a boring near and parallel to that for the reaction tube. Rapid heating (owing to the good conductivity) and constant temperature (owing to the mass) were thus obtained. The farther end of the tube should be inclined downward to prevent the reflux of condensed products. When a nickel-pumice catalyst is used it may be placed in a U-tube kept in an oil-bath. Heating may be by gas or by electric resistances.

704. Introduction of the Substrate. If the substance to be hydrogenated (substrate) is a gas, this may be introduced together with the hydrogen by any of a number of sufficiently obvious devices.

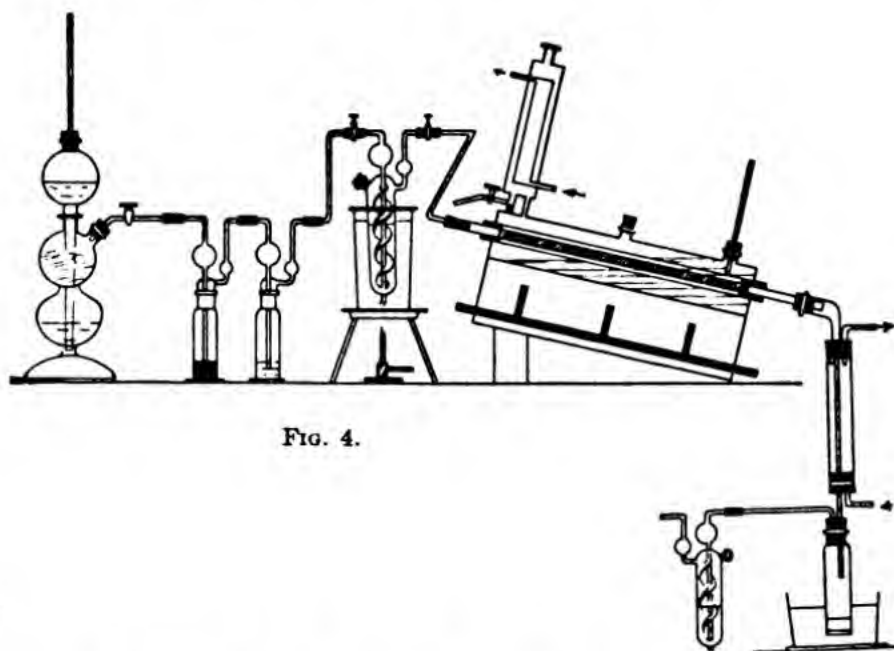


FIG. 4.

For liquids there are two methods. The simplest is to place the liquid in a distilling flask, heated or cooled according to the volatility and to carry it into the reaction tube and over the catalyst by bubbling the hydrogen through it. If it is desired to measure or control the quantity of liquid passing, it may be dropped from a burette passing through the cork of the flask. The hydrogen should be in excess. Sabatier seems to prefer what appears to be a less simple method. The first end of the reaction tube has a two-hole stopper. One hole is for the hydrogen tube. Through the other passes the horizontal arm of a bent capillary tube, whose vertical arm passes through a stopper in the bottom of a wide vertical tube containing the liquid. The flow of the liquid should be continuous and not in drops. The rate of flow depends on the bore of the capillary and on the head. These should, therefore, be adjusted according to the viscosity of the liquid.

705. When the substrate is solid, the method of introduction depends on its melting-point and on its volatility. If the distillation flask method cannot be used (and with proper lagging it can almost always be made to work satisfactorily), the substance may be placed in a porcelain boat inside the reaction tube.

706. Collection of Reaction Products. Gaseous products may be collected over water, etc., in gas holders in a pneumatic trough. Liquids may be condensed, the method depending on their volatility. For slightly volatile liquids a Woulff's bottle suffices. For highly volatile liquids a Y-tube with wide arms (in other words, a U-tube with a bottom tubulure) is used. The bottom arm passes through the cork of an inverted tubulated bell which surrounds the vertical arms and is filled with ice or a freezing mixture. The condensed liquid is collected from the vertical tube, the gases from the second vertical arm.

707. For liquids of intermediate volatility, an ordinary condenser suffices, with the obviously necessary means for permitting the passage of gas.

708. Solids are collected by prolonging the reaction tube and bending it down, the end being cooled.

709. Hydrogen. The hydrogen for laboratory purposes may be generated by the action of acid on zinc in one of the numerous forms of apparatus described in textbooks of chemical technique. In most cases, however, it is obtained from cylinders of the compressed gas. The cylinder should be furnished with a reducing valve and with pressure gauges. One gauge shows the pressure in the cylinder, and therefore indicates how much gas it holds; the other gives the pressure at which the reducing valve is delivering the hydrogen to the apparatus.

710. For most experiments in hydrogenation there is no need to purify the gas supplied in cylinders. It is almost invariably electrolytic hydrogen containing, at most, traces of oxygen. Hydrogen generated by the action of acids on zinc will sometimes require purification particularly if the zinc or the acid is impure. It may contain water, acid, hydrogen sulphide, arsine, phosphine or antimony hydride. All of these, if present, must be removed by a purifying train. First the gas passes through a tube of resistance glass, filled with copper turnings kept at a dull red heat: next comes a tube containing slightly moistened lumps of potassium hydroxide. It is not necessary to dry the gas⁴ but, if this is desired, it may be passed over calcium chloride.

711. Where hydrogenation is to be carried on at atmospheric pressure ordinary rubber tubing may be used for connections. In the course of rubber manufacture a number of substances are used which are deleterious to hydrogenation, e.g., sulphur compounds. Moreover there is, in some tubing, a good deal of dust. The tubing used in hydrogenation apparatus should be smooth inside and free from dust. The tubing should be boiled with alkali before use. Sulphur-free and pure gum tubing are in the market. As much of the connections as possible should consist of glass or metal tubing, brought, at junctions, to butt joints merely held together by rubber.

712. For hydrogenation under pressure special connections must be made. At really high pressure these must be of metal with union joints. At less pres-

⁴ Sabatier (tr. Reid). *Catalysis in Organic Chemistry*, para. 446.

tures, such as 2-3 atmospheres, armored hose or reinforced rubber and canvas tubing may be used.

713. When a brisk current of hydrogen is depended on for agitation it is not practicable to make a direct measurement of hydrogen absorption. This must, therefore, be controlled indirectly by taking samples and determining the iodine value, the melting-point, the refractive index, or some other measure of the degree of hydrogenation.

714. If it is desired to maintain the delivery of hydrogen at a constant value a flow meter may be interposed between the source of gas and the reaction vessel.

715. In certain cases, especially in organic syntheses by hydrogenation, it is important to measure, fairly exactly, the hydrogen absorption. For example it may be desired to limit the hydrogenation to the absorption of an amount of gas representing 1 atom added to the molecule. In such cases operation is usually conducted in a closed circuit.

716. The apparatus illustrated in Fig. 5 was

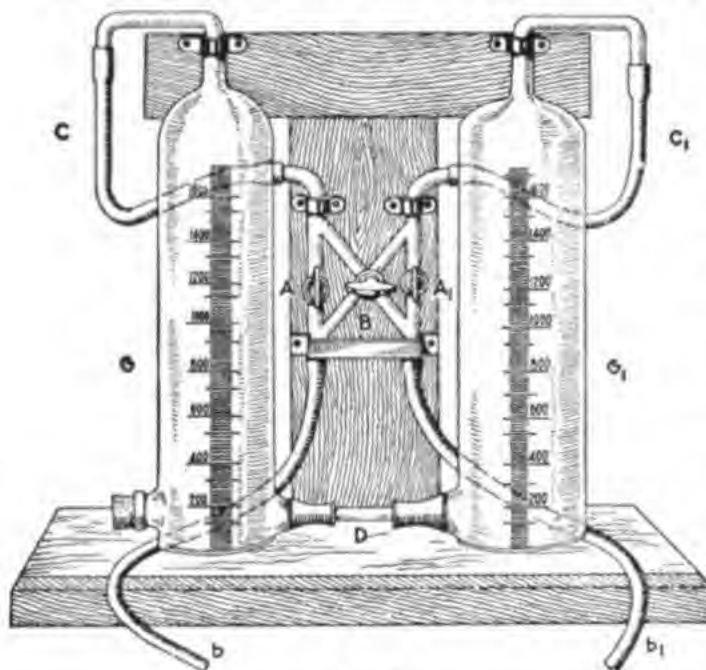


FIG. 5.

described by Voswinckel⁵ for measuring the hydrogen absorption when working at moderate plus pressures. In the form illustrated it is supplied by Bernhard Tolmacz and Co., of Berlin.

The two thick-walled graduated cylinders *G* and *G*₁ are drawn out at their necks in order to do away with the rubber stoppers that were employed in the originally designed apparatus. These elongated necks are bent in the form of an L and are connected with the valves *A* and *A*₁ by means of pressure tubing. Of the rubber tubes *b* and *b*₁, one connects the apparatus with a hydrogen tank, while the other joins the apparatus to a reaction vessel of the shaking type. The entire apparatus is mounted on a wooden frame to insure stability and render it easily transportable. The two cylinders which are joined by the glass tube *D* are filled with 1½ liters of water. By means of air or hydrogen the water is transferred into the cylinder *G*₁ until the latter is full. The valve *A*₁ is then closed to prevent the water from flowing back in *G*. The cylinder *G*₁ is connected with the hydrogen tank by means of *b*₁ and the water is displaced by hydrogen. Valve *A*₁ is again closed. The hydrogen tank is connected with *b*, valve *A* is opened and hydrogen is admitted until the pressure is about 1½ atmospheres. The cylinder *G* is then connected to the reaction chamber which has been previously evacuated. The valve *A*₁ is opened and the shaking machine is set in motion. When the hydrogen of the cylinder *G*₁ is used up, the cylinder *G*, which in the meantime has been filled with hydrogen, is connected with the reaction chamber and *G*₁ is connected to the tank of hydrogen. During

⁵ *Chem. Ztg.*, 1913, 489.

this operation the valves *A*, *A*₁, and *B* are all shut to prevent the water from flowing back from cylinder *G*₁ into cylinder *G*.

717. It may be necessary to guard against the admission of even a trace of air into the apparatus during a hydrogenation. In such a case Stark's apparatus ⁶ may be useful.

718. It consists of a glass vessel with two necks, each provided with a glass stopcock. A small funnel with a stopcock is fused into the upper part of the vessel between the two necks. One neck is connected with the source of hydrogen, the other with a graduated gas burette and mercury reservoir. The substance to be reduced is placed in the glass vessel and a current of hydrogen passed through. At this stage the burette and reservoir contain no mercury. The hydrogen supply is then cut off and mercury is poured into the reservoir from which it flows and partly fills the burette. By lowering the reservoir a solution of platinum or palladium can be introduced through the funnel with the stopcock without admitting any air.

719. When such precautions as these are necessary, evidently the last trace of oxygen must be removed from the hydrogen used. This may be done by passing the gas over heated nickel or palladium,⁷ or red hot copper followed by a drying tube containing solid caustic potash.⁸

720. Hydrogen containing water vapor cannot be completely freed from oxygen by passing over hot copper or tungsten, because the reaction with water is reversible. The removal with sodium has inconveniences in practice. But if the gases are passed over metallic chromium at 750° to 850° C., the oxygen is completely removed.⁹

721. For work in the vapor phase the apparatus of Sabatier and Senderens ¹⁰ may be used, especially where it is important to control exactly the amount of unsaturated material sent through in a given time. For most purposes, however, a simpler outfit will suffice. Such a one is described and illustrated in Maxted: *Catalytic Hydrogenation and Reduction* (Philadelphia, P. Blakiston & Co., 1919).

722. For an excellent example of precise experimental hydrogenation in the vapor stage the reader should consult the paper by Dougherty and Taylor ¹¹ on the hydrogenation of benzene. The results are of considerable theoretical importance. The methods employed for attaining the high degree of precision required will repay study. The following problems are dealt with: (1) Purification of hydrogen. (2) Measurement of flow. (3) Obtaining a definite ratio of vapor to hydrogen. (4) Manometric determination of the amount of hydrogen absorbed. (5) Influence of water vapor, of carbon monoxide and of hexahydrobenzene.

723. An unusual method of effecting catalytic hydrogenation in the gas phase is that used by Rather and Reid ¹² in an attempt to investigate quantitatively the reaction between hydrogen and ethylene. Instead of exposing a fixed surface of catalyst to the reaction gases, these workers suspended the catalyst

⁶ *Ber.*, 1913, **46**, 2335.

⁷ Maxted: *Catalytic Hydrogenation*, p. 23.

⁸ Sabatier, *loc. cit.*, 346.

⁹ Brit. Pat. 284,808, Nov. 25, 1926, to General Electric Co. and Smithells; *Chem. Age* (London), 1928, **18**, 224.

¹⁰ See Fig. 1 and description.

¹¹ *J. Phys. Chem.*, 1923, **27**, 533.

¹² *J. Am. Chem. Soc.*, 1915, 2115.

in an inert liquid (melted paraffin wax). Vigorous agitation was applied as the reactant gas mixture passed through it. There is a slight suggestion here, in the object sought, of recent proposals to effect gas reactions in the presence of catalyst dust suspended in the gases.¹³

724. Preparation of the Catalyst.¹⁴ One hundred grams of infusorial earth were treated with a solution of 50 g. nickel nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in about 150 cc. water, and the resulting moist mass added to a strong water solution of 60 g. sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, to precipitate the nickel as carbonate. The product was well washed and dried and the nickel carbonate reduced by heating, in a glass tube, just below red heat, in a current of pure dry hydrogen till no more water was formed, and cooled in a current of pure dry carbon dioxide. In order to standardize the catalyst, its activity was tried with cottonseed oil, 70 g. of the oil and 1 g. of the catalyst being treated with pure dry hydrogen at 180° . The iodine number of the oil was lowered, in sixty minutes' treatment, from 113.7 to 44.6. Experiment showed that the catalyst did not deteriorate appreciably during the time that each portion of it was in use.

725. Temperature. In all of the experiments, the temperature was maintained at $180^\circ \pm 1^\circ$ by immersing the bulb of the reaction-flask in an oil-bath, the temperature of which was maintained constant by an oil thermostat with mercury contacts, controlling a gas regulator.

726. Materials. The ethylene was made according to method of Senderens and washed with sodium hydroxide solution. The hydrogen was from zinc and acid and was washed with alkaline potassium permanganate. As an inert medium, in which to suspend the catalyst, melted paraffine was used.

727. Procedure. The gas mixtures were prepared in gasometers, holding about 24 l., which were provided with an arrangement for maintaining nearly constant pressure. The same lot of the mixture was used for the whole series of experiments on any one proportion. Each mixture was analyzed for ethylene by the usual method with fuming sulphuric acid. The mixture of gases was run through concentrated sulphuric acid to dry it and then into the reaction flask which contained, in each experiment, 1 g. of the catalyst, and 70 g. of the paraffine. The stirrer was run at 3300 to 3500 r.p.m. In each case, time was allowed for the displacement of air from the apparatus and for the hot paraffine to come to equilibrium with the ethylene, hydrogen, and ethane passing through it. The attainment of this equilibrium was shown by constancy in the analysis of the successive samples of the issuing gases. The amount of ethane in the product, which is the same as the percentage of reduction of the ethylene, was calculated by the following formula, in which E_1 is the percentage of ethylene in the original mixture and E_2 is the percentage of ethylene in the products of the reaction.

$$\text{Ethane} = \frac{100E_1 - 100E_2}{100 - E_2}.$$

Fresh lots of catalyst and paraffine were used for each 24 l. of mixture. The rate of gas flow and the composition of the original mixture are the only variables studied. The results are by no means as regular as could be wished, and some are evidently out of relation to the others. They are not to be considered as final. The irregularities may depend on factors not as yet known or controlled. In Fig. 6 the percentage of the ethylene reduced is plotted against the rate of flow. The interesting result is that, for all of the mixtures, about 70 per cent of the ethylene is reduced when the rate of flow is 10 cc. per minute. All of the results for the 10 per cent mixture are regular and as would be expected. Those for mixtures containing higher percentages of ethylene are by no means so regular and the curves are in unexpected relations to each other. Doubtless the determining factor is solubility. The reaction is probably taking place between the ethylene and the hydrogen that are dissolved in the paraffine. The mass law then holds for this solution and not for the gases that are not in solution. When the passage of the gas mixture is rapid, the gases are swept through before equilibrium can be established between the gas mixture and the solution.

728. In Fig. 6 the volume, in cubic centimeters, of gases made to combine, per minute, is plotted against the rate of flow. As was to be expected, this amount increases with the

¹³ See para. 4826. Note also 4701, 4702, 4714 and 5035.

¹⁴ *J. Am. Chem. Soc.*, 1915, 2115.

amount of the gas mixture that is exposed to the action of the catalyst. The results for the different mixtures are in the expected order, those for the rate of 100 cc. per minute being the most instructive. Under these circumstances, in the 50 per cent mixture, 17 cc. of hydrogen is made to combine with 17 cc. of ethylene in one minute. Since the 1 g. of the catalyst, as prepared, cannot contain more than 0.1 g. nickel, the volume of this, considered as Ni, would be about 0.01 cc. or less. Hence the catalyst induces the reaction in 3400 times its own volume of the gas mixture in one minute. In the experiment with cottonseed oil, given above, the same amount of nickel caused the absorption of 4230 cc. of hydrogen or 423,000 times its own volume of hydrogen in sixty minutes, or 7000 times its own volume in each minute. These volumes are calculated for a temperature of 0° and would be 67 per cent greater at 180°, at which the action really took place. The amount of hydrogen caused to combine with the oil is several times as great as the amount combined with the ethylene, which is as would be anticipated, as the concentration of the ethylene in the paraffine is probably much smaller than the concentration of the olein in the oil, and the partial pressure of the hydrogen in the mixture is only half so great as in the pure hydrogen. However, the results are of the same order of magnitude.

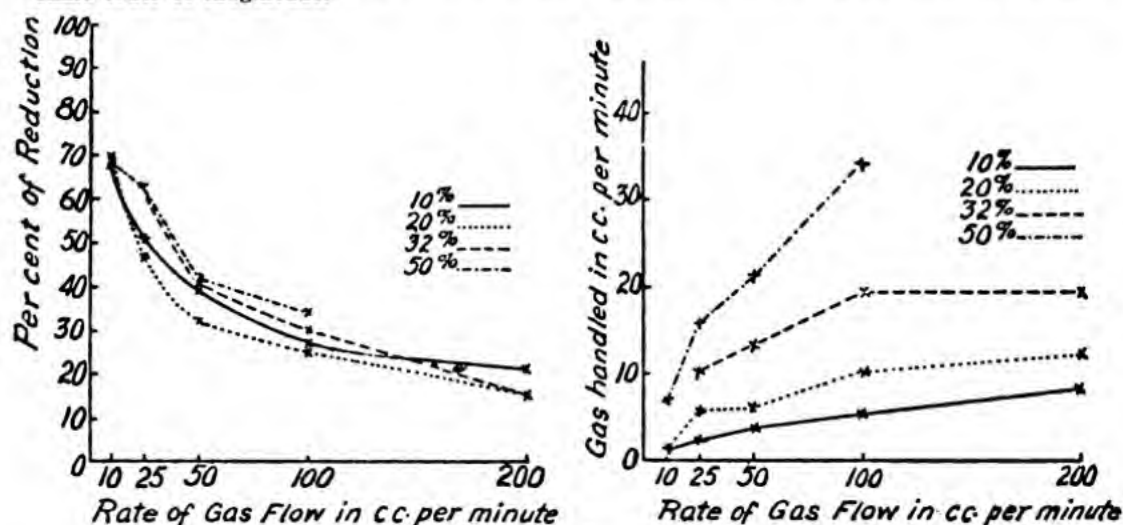


FIG. 6.

LIQUID PHASE

729. For hydrogenations in the liquid phase at atmospheric pressure the apparatus may be of the utmost simplicity. In the author's laboratory one method of preparing small quantities of hydrogenated oils needed for various researches has involved the use of apparatus which could scarcely be simpler. For example if it be desired to prepare a kilogram of hydrogenated castor oil, we proceed as follows:

730. A dry round-bottomed flask of 1½ to 2 litres capacity, with a 2-hole cork, is set in an oil-bath in which is a thermometer. In it is placed nickel formate, 31 gs. (this gives about 10 gs. nickel for 1 kilo oil). Through one hole in the cork passes a hydrogen delivery tube ending just over the formate; through the other passes a thermometer which touches the bottom of the flask. The cork is loosely fitted. The hydrogen is now allowed to flow at a rate such that it slightly disturbs the formate. Heat is applied to the oil-bath: usually the inside thermometer lags some 15° or 20° C. behind the thermometer in the oil. When the former marks about 240° C. the formate decomposes rapidly but quietly. In a few minutes it is completely reduced. The heat is cut off and the nickel is allowed to cool, *without interruption of the hydrogen*. This is because the catalyst is pyrophoric, and access of air would ruin its catalytic activity. When the temperature reaches, say, 100° C., the thermometer is

withdrawn and a long-stemmed funnel replaces it. Through this the oil to be hydrogenated, preheated or not, is introduced, the current of hydrogen being steadily maintained. The funnel is withdrawn, the thermometer replaced, the heating renewed and maintained at the desired temperature of hydrogenation. The current of hydrogen maintains the catalyst in suspension and effects all the agitation necessary.

731. When hydrogenation is complete, the separation of the nickel may be effected either by filtration (in a jacketed funnel or in an oven) or by centrifuging. The former is simpler, but if a centrifuge permitting of keeping the oil hot is available, centrifuging is in every way preferable and quicker.

732. The method of preparing the nickel catalyst which we have just described is offered, not as that which produces the most active catalyst, but as the simplest, especially adapted for extemporizing. The catalyst so formed is of good activity and is easy to filter. It does not show any marked tendency to form nickel soaps with ordinary oils under usual conditions of hydrogenation and, according to De Roubaix¹⁵ catalyst thus made forms very little nickel oleate and no stearate when used for hydrogenating even oleic acid.

733. Description of the Apparatus and Technique for Experimental Hydrogenation with the Adams Platinum-oxide Catalyst.¹⁶ This apparatus may be regarded as the latest development of Skita's shaking apparatus. A ready-made commercial form is described and illustrated in paras. 740-741.

734. A. The Apparatus. As a container for hydrogen a strong tank *A* of about 8-10 l. capacity is used. The top of the tank contains two openings *B* and *C*. In one of these *B* is welded a tube holding a gauge and valve, through this tube the hydrogen from a large cylinder *D* is introduced into the tank. In the second opening *C* is welded another tube controlled by a needle valve with two outlets, *E* and *F*, each of which holds a needle valve. *E* is used for the vacuum, a manometer *G* being introduced into this system, and *F* for a tube leading to the reaction mixture bottle *H*. These outlets are so arranged that it is possible to shut off the tank from either outlet and also to make a direct connection between the vacuum and the bottle *H*, leaving *A* out of the circuit. The connection between the tank *A* and the bottle *H* is a heavy taped rubber tube (Note 1), which is in turn connected to a glass tube inserted through the stopper of the bottle. The rubber tube and stopper should be high-grade and must be carefully boiled with alkali before being used (Note 2). The arrangement for shaking the bottle is shown in the diagram. A metal strip *I* is clamped tightly over the stopper in order to hold the stopper in the bottle when the latter is filled with hydrogen under pressure.

735. For some reactions it is advantageous to heat the mixture and the following arrangement is satisfactory. The bottle *H* is wrapped with moistened asbestos paper to a thickness of about $\frac{1}{4}$ inch; the paper then allowed to dry. When the asbestos is thoroughly dry the bottle is wound with a coil of nichrome wire, beginning the coil at the bottom of the bottle and making the turns about $\frac{3}{8}$ inch apart. The wire is then covered with a $\frac{1}{8}$ -inch layer of asbestos, which is moistened and allowed to dry, after which the wire is wound around the bottle in another coil from top to bottom. The second coil is covered with asbestos as before, and the ends of the wire are connected to the terminal wires from a source of current. These wires are led along the bottle to the neck and held by means of tape in order to avoid excessive shaking. A variable resistance in the circuit is used to regulate the temperature.

736. B. Use of the Apparatus. The tank *A* is filled with hydrogen to a pressure of 40-45 lbs. from the cylinder *D* (Note 3). The solution, in a suitable solvent, of the substance to be reduced is poured into the bottle *H* and the platinum oxide is added (Note 4). The bottle is attached to the apparatus and evacuated by opening valves *E* and *F* and closing *C*. In the case of low-boiling solvents, the evacuation is continued only until the solvent begins to boil; in other cases it is continued until the pressure as recorded by the manometer remains fairly constant. The valve *E* is then closed and hydrogen is admitted to the bottle *H* from

¹⁵ Cf. para. 566.

¹⁶ This description was kindly furnished by Professor Adams and is essentially that which is published in *Organic Syntheses*, 8, p. 10 *et seq.*

the tank *A* by opening valve *C* (Notes 5 and 6). When the pressure in the bottle has become adjusted the pressure of the hydrogen and the temperature of the tank *A* are recorded. Shaking is started. Within a few minutes the brown platinum oxide turns black and the absorption of hydrogen begins. The shaking is continued until the theoretical amount of hydrogen is absorbed. The hydrogen remaining in the bottle is removed, air is admitted, and the mixture allowed to stand, or if necessary shaken for a few minutes in order to aid the settling of the catalyst.

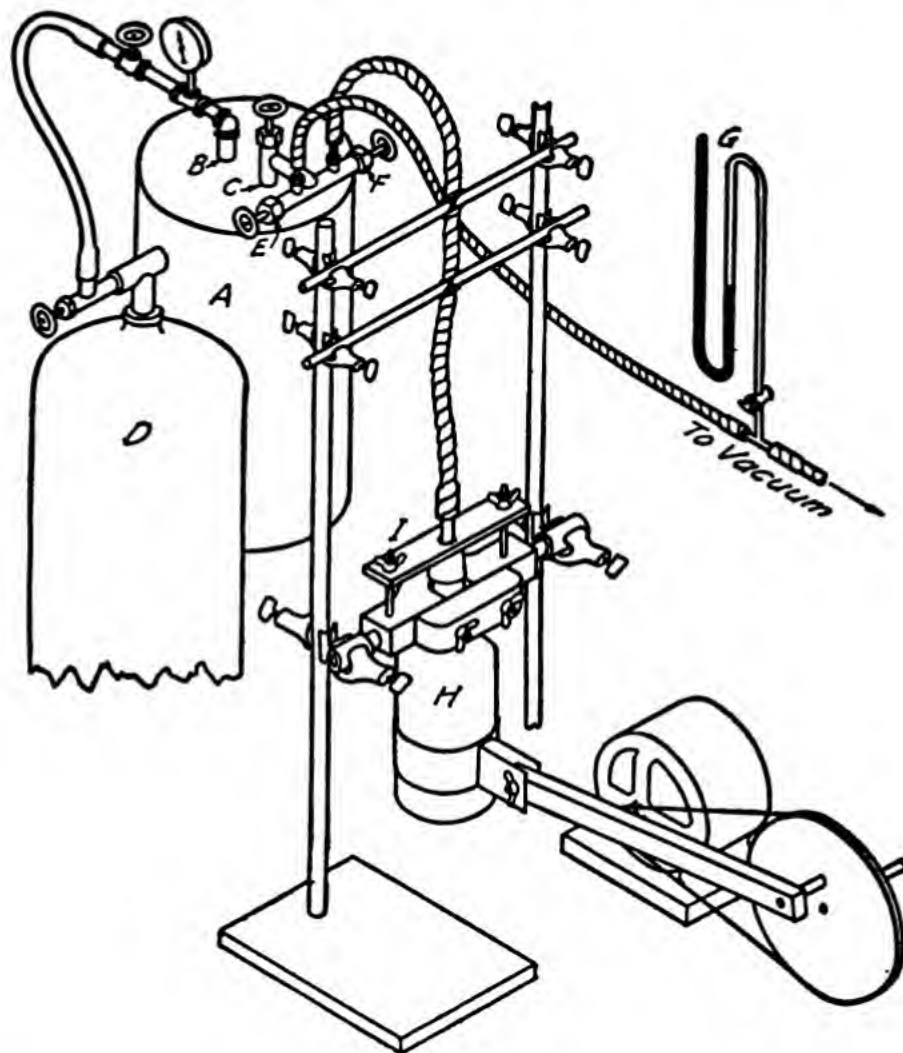


FIG. 7.

737. In certain cases where the catalyst settles spontaneously at the end of the reduction it is not necessary to shake the mixture with air. The solution may be decanted from the main portion of the catalyst and a second reduction carried out. In cases where the catalyst cannot be used directly for another reduction the solution is filtered, preferably through an asbestos filter (Note 7) and fresh solvent is used for washing. The reduction product is isolated from the filtrate, usually by distilling off the solvent.

738. C. Standardization of the Apparatus. The hydrogen tank may be standardized by reducing 11.6 g. (0.1 mole) of pure maleic acid (Note 8) dissolved in 150 cc. of 95 per cent alcohol, using 0.1 g. of catalyst. The reduction is carried out according to the procedure described above in *B*. Shaking of the mixture is continued until no more hydrogen is

absorbed; the theoretical amount is absorbed by 0.1 mole of maleic acid within twenty or thirty minutes. The temperature of the tank is recorded. The decrease in pressure corresponds to 0.1 mole of hydrogen at the observed temperature and pressure.

739. Notes. 1. A copper tube may be used for this connection but is less satisfactory since the shaking tends to wear it out at the joints.

2. It is advisable to boil the tube and stopper with several portions of 20 per cent sodium hydroxide until the solution is no longer colored yellow, after which the boiling is carried out several times with distilled water.

3. Electrolytic hydrogen was used in all experiments. This hydrogen is essentially free from all impurities except oxygen. Since oxygen in general has no harmful effect upon the reductions, no purification is necessary. If, however, oxygen-free hydrogen is needed, the gas must be passed over heavy platinized asbestos.

4. This procedure may be varied in certain cases where it seems advantageous to reduce the platinum oxide to platinum-black in the presence of the solvent alone.

5. During the reductions it is usually advisable not to allow the pressure in the tank *A* to drop below about 25 lbs. if the reduction is to be carried out in minimum time. When the gauge registers 25 lbs. the tank is closed off from the reducing bottle and the pressure is increased to about 40 lbs. by the admission of more hydrogen from *D*.

6. Ordinarily traces of air in the hydrogen have no deleterious effect upon the reductions. If in any experiment absolute freedom from air is desired, the bottle may be evacuated and refilled with hydrogen two or more times. In this way the air is all washed out of the bottle.

7. When paper filters are used the rapid suction of air through the paper in the presence of the catalyst often causes spontaneous combustion of the filter. Paper filters may be used, however, if care is taken to keep the filter covered with solvent while suction is being applied; just before the last portion of solvent has run through the suction is stopped.¹⁷

8. Instead of maleic acid, 10.6 g. (0.1 mole) of pure benzaldehyde may be used for the standardization. In this case 1 cc. of 0.1 molar ferrous sulphate is added to the mixture of benzaldehyde, alcohol and catalyst before the reduction is started. The reduction is complete in fifteen to thirty minutes.

740. The experience gained by Adams and his associates at the University of Illinois has been embodied in a compact and convenient apparatus for catalytic hydrogenations.

741. This apparatus, which is made by the Burgess-Parr Company, of Moline, Ill., is illustrated by Fig. 8. It consists of an agitating mechanism, power for which is derived from a $\frac{1}{10}$ -h.p. motor, and which keeps in constant turbulence the reactants. The catalyst, solvent, and compound are confined in a 1-pint bottle made of flint glass, with a mouth of $\frac{1}{8}$ -inch diameter. A guard covers the bottle to protect the operator from accidental explosion. A rubber stopper seals the mouth of the bottle and permits any pressure up to 3 atmospheres. Pressure is maintained by connection to a supply tank with a capacity of approximately 850 cu. ins. The tank is of seamless brass tubing with bronze headers, and is tested for a pressure of 150 lbs. per sq. in. The entire instrument is mounted on a heavy base. By previous calibration of the apparatus, the drop in pressure, measured by means of the gauge attached, affords a quick and accurate method of measuring the rate of the reaction and also the extent to which the reaction in the bottle has proceeded. The apparatus may also be used for any reactions which require vigorous agitation, and is especially valuable for maintaining an inert atmosphere.

742. An apparatus has been devised by E. Emmet Reid¹⁸ and used for the study of catalytic hydrogenation. The problem is to introduce a high-speed stirrer, inlet and outlet tubes, and, possibly, a sampling tube through a comparatively small stopper and to render the whole gas-tight for both increased and reduced pressure. The apparatus is shown in the sketch in section, Fig. 9.

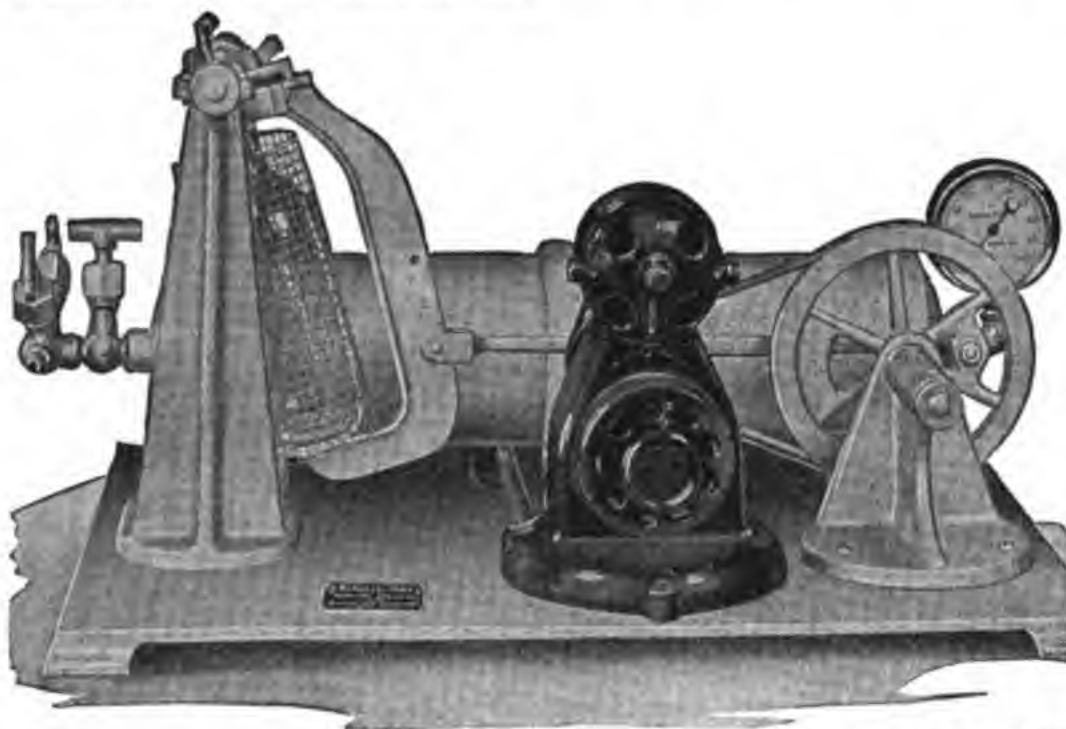
743. The bearing *AC* is made of two pieces of steel rod, *AB* and *BC*, 0.5 and 1.5 ins. long, respectively. Both of these have a $\frac{1}{8}$ -in. hole drilled longitudinally through them, then the

¹⁷ It is feasible and often more convenient to effect the separation with the centrifuge.

¹⁸ *J. Am. Chem. Soc.*, 1915, 2112.

longer one is drilled out to a size of about $\frac{1}{8}$ for most of its length, i.e., from *B* to *D*. The shorter piece is turned down for half its length till it fits closely into the other, so that a double bearing is formed, with an enlarged cavity in the central portion. The two parts are assembled and channels about $\frac{1}{8}$ by $\frac{1}{8}$ in. are cut in opposite sides, as shown at *J* and *K* in cross-section in Fig. 8. Care must be taken that the channels do not cut through the walls of the cavity. The $\frac{1}{8}$ brass tubes that are used for the gas inlet and outlet tubes are laid in these channels, which are then filled with solder, the solder more than filling the channels. The excess of solder is turned off in the lathe so that the whole is a perfect cylinder externally and adapted to make a tight joint when passed through a cork.

744. The stirrers may be of any suitable form, but the Witt centrifugal stirrer shown is one of the best, as when run at high speed it effects very thorough mixing. The stirrer may be made of glass and fastened to the shaft by a bit of wire which passes through a hole in the shaft and through holes in the stirrer. The shaft *S* is of $\frac{1}{8}$ -in. drill rod and carries a pulley of suitable size. The inlet and outlet tubes are bent as shown and carry enlargements so as to make convenient joints with rubber tubing.



(Courtesy Burgess-Parr Co.)

FIG. 8.—BURGESS-PARR CATALYTIC APPARATUS WITH VARIABLE SPEED MOTOR.

745. The bearing passes through a hole in a 0.5-in. rod *F*, and is held in place by a set screw *G*. This rod is conveniently clamped to a laboratory iron stand.

746. To assemble the apparatus, the shaft is pushed a short distance into the bearing from the bottom and mercury is poured in. The shaft is then pushed on through, causing the excess of mercury to overflow and leaving the cavity in the bearing filled with mercury. Thus a gas-tight mercury seal is formed which is tight no matter how fast the shaft rotates. To make a stuffing-box gas-tight would require so much pressure that the rotation of the shaft would be hindered. The mercury seal, though tight, offers no resistance to the motion of the shaft. This seal is tight against either excess or diminished pressure for moderate pressures. The apparatus in use proved to be gas-tight under a pressure of 3 ft. of water. The shaft must fit the bearings very accurately to avoid danger of loss of mercury, but little trouble has been met with in this respect. Lubrication is accomplished by placing a drop of oil above and below the bearings and working the shaft up and down a few times. This should be done each time the apparatus is used.

747. In case it is desired to take out samples during the course of the reaction, the bearing is cut from a somewhat larger rod, and a hole is drilled through the assembled bearing, to one side, as shown in section at *H* in Fig. 11. This hole is stopped by a plug lubricated with oil. For taking out a sample, a piece of 0.25-in. glass tubing is drawn out to a capillary about 6 ins. long. This is passed down through the hole in the bearing and the desired amount of liquid drawn out. A hole is drilled in the web of the pulley so that it can be brought over the hole in the bearing and allow the capillary to pass. In studying the velocity of the reaction, the

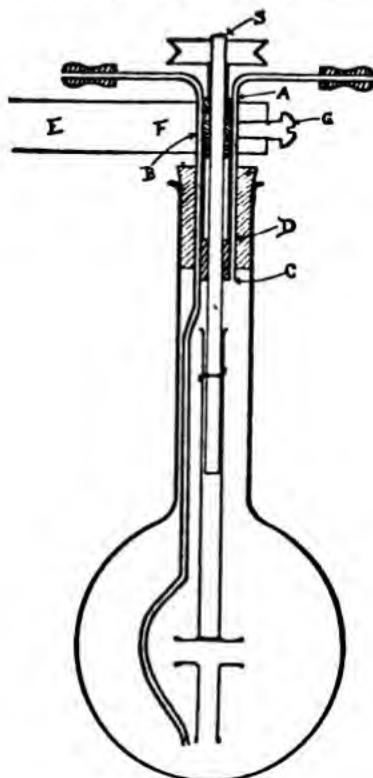


FIG. 9.



FIG. 10.



FIG. 11.

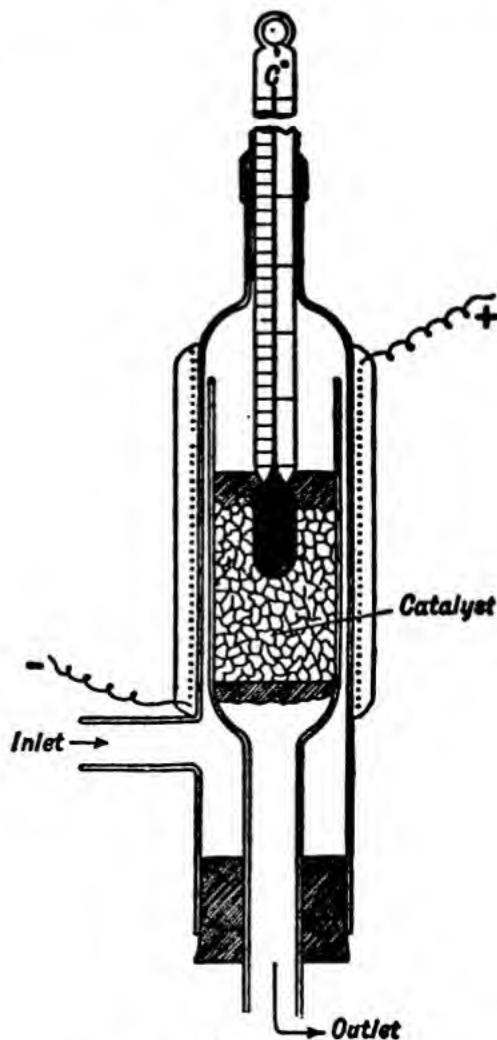


FIG. 12.

time is taken till the moment that the stirrer is stopped. Taking out a sample requires about one minute. The time for the next period is taken from the moment that the stirrer is again started. Experiments have shown that reactions of this sort, depending on stirring, stand practically still when the stirrer is not in operation.

748. The size apparatus here described has proved extremely useful for small-scale work of a variety of kinds. Obviously, the same plan might be used for apparatus for larger operations. The flask is heated to any desired temperature by being placed in a suitable bath. Temperatures up to 220° have been used. The stirrer has been run by an electric motor, a rubber band serving as a convenient belt. Speeds of 3000 to 4400 r.p.m. have been obtained without difficulty.

749. Rideal and Taylor ¹⁹ describe a compact and relatively simple apparatus for vapor phase hydrogenations, particularly suitable for studying temperature effects. The construction is shown in Fig. 12.²⁰ The outside tube is electrically heated. The upper end of the tube terminates in a tube of narrower bore to carry the thermometer or thermo-couple. The catalyst is contained in an inner concentric tube. There is between this and the outer tube an annular space through which the gases pass up and are heated. This apparatus is simple and permits of accurate temperature control. *Mutatis mutandis*, made of metal, it can be used for operations on a semi-technical scale.



FIG. 13.

750. Laboratory Autoclave for Hydrogenation. The illustration, Fig. 11, shows a laboratory type of autoclave for hydrogenation under pressure, made for the author by the F. J. Stokes Company of Philadelphia. The autoclave is of cast steel with a rounded bottom. The stirrer is operated by a round belt on a grooved pulley. Hydrogen inlet pressure gauge and safety valve are provided. The autoclave is guarded by a sheet-iron mantle and is heated by a gas burner.

751. Descriptions of apparatus and technique for operation under high pressures will be found in Chapter LII.

752. Combined catalytic-electrolytic method of reduction.²¹

The apparatus consists of a round-bottomed vessel which can be suspended so as to permit continuous agitation and through which a current of hydrogen or other gas can be

¹⁹ *Catalysis in Theory and Practice*, 2d ed., pp. 96-97.

²⁰ Rideal and Taylor, *loc. cit.*, by courtesy of The Macmillan Co.

²¹ Ishiwara, *Ber.*, 1924, 57, 1125, *J.S.C.I.*, 1924, 768B.

passed. It is pierced near the base by a hole which is provided with a rubber stopper through which a palladium cathode passes. Another opening in the top of the vessel carries a small porous pot containing dilute hydrochloric acid and a nickel anode. During reduction a current of hydrogen is passed into the vessel. The reducing action of the catalyst appears to be strengthened greatly by the passage of the electric current, but reduction is also effected in part directly at the cathode.



FIG. 14.—GOUGH & KING APPARATUS FOR CATALYTIC HYDROGENATIONS BY ADAMS METHOD.

The apparatus consists of a standard hydrogen cylinder *A*, fitted with a high-pressure automatic regulator with two gauges, the lower one indicating the pressure in the cylinder, and the upper the outlet pressure, which latter can be adjusted to give any constant outlet pressure from about 20 lbs. per square inch upwards. The outlet is connected by pressure tubing reinforced with canvas, to a valve *B* screwed and sweated into the shoulder of the cylinder *C*, which is an old hydrogen cylinder, capacity 9.97 litres, and no longer of suitable strength for the standard filling pressure of 120 atmospheres, but withstanding 10 atmospheres. A pressure gauge, graduated in divisions of 2 lb. per square inch, is screwed and sweated into the shoulder at another point, and can be read to within 0.5 lb. per square inch, thus being capable of indicating a minimum consumption of 0.03 g. of hydrogen at a working pressure of 3 atmospheres (absolute). The neck of this cylinder has a two-way connection, each carrying a fine adjustment valve. One of these may be connected to a vacuum pump, and the other to the hydrogenation flask, which can be shaken by means of an eccentric attached to a small motor. (*J.S.C.I., Chem. & Ind.*, 1928, 47, 410.)*

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753. Constable. Apparatus for investigation of catalyst poisoning. *Proc. Cambridge Phil. Soc.*, **22**, 738 (1925).
754. Klimont, *Chem. Zeit.*, 1922, **46**, 275; *J.S.C.I.*, 1922, **41**, 300A. Description of apparatus for hydrogenation at ordinary pressure. Requires special glass-blowing and possesses no obvious advantage over apparatus which can be extemporized from standard glassware.
755. Hughesdon, Robertson and Read (*J.S.C.I.*, 1929, 263T) describe two types of circulatory apparatus used by them in the hydrogenation and dehydrogenation of piperitone, menthone, isomenthone and a number of related substances (*J.C.S.*, 1923, **123**, 2924; *Sydney Univ. Sci. J.*, 1923, **7**, 24; and unpublished researches). Both forms of apparatus are based on the general principle of Morgan's simple circulating pump (*J.C.S.*, 1915, **107**, 1710).

* Courtesy Journal of the Society of Chemical Industry.

CHAPTER VIII

NON-COLLOIDAL NOBLE METAL CATALYSTS

800. The noble metal catalysts used in hydrogenation are generally members of the platinum group, i.e., platinum, palladium, iridium, rhodium, ruthenium, osmium, and especially the two first mentioned.

801. Platinum was one of the first catalysts to be used in experimental hydrogenation, and, with palladium, it still occupies an important place in laboratory practice. Although most industrial hydrogenations are performed with the aid of nickel catalysts, there still remain some which call for the use of the noble metals. The advantage usually sought in such cases is the possibility of hydrogenation at low temperatures, frequently at "room temperature." The relative importance, in industry, of the two classes of hydrogenation catalysts, i.e., noble metal and base metal, may be roughly gauged by the number of inventions classified under these two heads, respectively, in the patent literature.

802. Noble Metal and Nickel Catalysts, Comparative Study. Zelinsky and Turova-Pollak¹ have studied the activity of noble metal catalysts and of various nickel catalysts in the hydrogenation of benzene (and in dehydrogenation of cyclohexane). The noble metal catalysts were all prepared by one method, namely, by soaking asbestos in a solution of the chloride, then in 35 per cent formaldehyde, then in 50 per cent caustic potash solution, washing thoroughly in water containing a little acetic acid and drying at 120° C. The nickel catalysts were made by six different processes and numbered accordingly. I. Nickel chloride was treated with formaldehyde and potassium hydroxide; the product was reduced in hydrogen at 300°–350° C. II. Nickel carbonate was reduced at 310°–320° C. III. Nickel powder was heated in hydrogen at 310° C. IV. Asbestos, impregnated with nickel nitrate solution, was ignited and treated with hydrogen at 310° C. V. This catalyst was made by Sabatier's method, calcining the nitrate and reducing the oxide at 300° C. VI. Nickel deposited on clay.

803. Platinum, iridium, rhodium, and ruthenium cause the conversion of benzene into cyclohexane within wide limits of temperature (100–180°). At 200–210°, dehydrogenation occurs to some extent even in the presence of hydrogen, except in the case of iridium. Palladium is a somewhat less effective hydrogenating catalyst, the full activity of which towards benzene is not developed below 155–180°. Nickel black I is a very efficient hydrogenating catalyst at 100–210°, whereas nickel II and III are feeble and useless, respectively. Nickel IV is active at about 130°, nickel V between 130° and 180°, whereas nickel VI has the optimum temperature 175–180°. At 250–260°, palladium, platinum, iridium, and rhodium still cause hydrogenation of benzene, whereas ruthenium is almost inactive. At 300–310°, hydrogenation

¹ *Ber.*, 1925, 58B, 1298; *J. Chem. Soc.*, 1925, 128, i, 1052.

tion is observed with platinum and rhodium, scarcely with palladium, and inappreciably with iridium and ruthenium. Nickel catalysts I, IV, and V cause marked hydrogenation at 250–260°, whereas catalysts II and VI are feebly active. All nickel preparations lose their power of causing hydrogenation at 300–310°. It therefore appears that the specific properties as a reducing catalyst towards benzene attributed to nickel by Sabatier and Senderens are not peculiar to this metal, which can frequently be replaced advantageously by platinum or palladium. The noble metals are less liable than nickel to cause secondary decompositions.

804. The Alleged Dependence of Hydrogenation Catalysis on the Presence of Oxygen. The *locus classicus* for the affirmative in this controversy is the paper by Willstätter and Waldschmidt-Leitz.² This article is highly dogmatic in tone and some of its conclusions have been traversed and, apparently, discredited. Nevertheless its importance is great.

805. Willstätter and Jaquet³ were led to the conclusion that platinum itself, and platinum loaded with oxygen are to be regarded as distinct catalysts. It is now shown, however, that platinum and palladium, whether as spongy metal or as colloid, are incapable of bringing about the hydrogenation of even the most reactive olefines if they have been freed completely from oxygen.

806. The catalyst may be freed completely from oxygen by treating its suspension in glacial acetic acid with hydrogen for thirty hours at the atmospheric temperature, or eight hours at 50–60°. It is then completely insoluble in hydrochloric acid, and does not liberate iodine from acidified potassium iodide solution. It is incapable of causing the hydrogenation of benzene, cyclohexene, limonene, or pyrrole, but acquires this power if shaken for a short period with air. Deoxidation of the catalyst takes place during hydrogenation, and the "poisoning" action of certain substances, such as glycerol and thiophen, is certainly due to this cause, but it is doubtful [sic] if all cases of paralysis of the catalyst can be explained by the removal of oxygen. Removal of oxygen by diminution of pressure can be accomplished with difficulty, but, by continuous exhaustion with a high vacuum pump, it was found possible to get a nearly inactive preparation.

807. Hydrogenation of a di-olefine could not be effected in the presence of palladium-black which had been freed completely from oxygen, while oxygen-free colloidal palladium was also found to be inactive.

808. Catalytic hydrogenation in the presence of nickel preparations has been regarded by Sabatier as exclusively a property of the metal; the function of the oxides of nickel has, however, been recognized by Bedford and Erdmann, while Brochet has expressed the opinion that pure nickel is catalytically inactive. The experiments of Willstätter and collaborators show that while nickelous oxide and nickel suboxide are active, the metal itself, even when prepared at the lowest possible temperature, is inactive in the presence of sodium cinnamate, oleic acid, or methyl oleate, but acquires activity when primed with oxygen, the quantity of the latter which is required being very small.

809. The discovery of the rôle of oxygen in catalytic hydrogenations in the presence of platinum enables the technique of the operation to be improved considerably, since the catalyst is reactivated by oxygen as soon as it shows signs of diminished activity, and "poisoning" is circumvented either by increasing the amount of platinum or by suitable treatment with oxygen. Priming is particularly useful when only small quantities of catalyst are used or when it is employed frequently. The use of spongy palladium has no advantage over that of platinum, while, on the other hand, the greater absorption capacity of the former for hydrogen renders more difficult its reactivation by oxygen to such an extent that the procedure becomes either dangerous or cumbersome. According to Boeseken and his co-workers, the process of catalytic reduction by finely divided metals depends on a diffusion phenomenon which precedes the actual hydrogenation and controls the rate of reaction, since it is assumed to take place more slowly than the actual reduction. This hypothesis does not explain the very different rates of hydrogenation of benzene and cyclohexene under similar conditions, since it is improbable that the diffusion process can differ greatly in the two cases, or the cessation or delay after addition of a molecule of hydrogen to cinnamic acid. It appears more probable that the rates observed in catalytic hydrogenation depend on two fac-

² Ber., 1921, 54B, 113. Our abstract is abbreviated from *J. Chem. Soc.*, 1921, 120, ii, 185.

³ Ber., 1918, 51, 767.

tors: (a) the actual velocity of hydrogenation, and (b) the decrease in the amount of catalyst, since the spongy or colloidal metal, which contains oxygen, is reduced to the inactive metallic hydride, while it transfers hydrogen to the substance under investigation. Since the loss of oxygen from the catalyst frequently seems to take place with uniform rapidity, it is possible to compare the activities of unsaturated substances by comparison of the volumes of hydrogen which are transferred to them by a given weight of oxygenated platinum before the latter becomes exhausted. Alternately, the initial rates of hydrogenation may be compared. The results obtained by the two methods are similar.

810. Substances may be divided into three groups, according to their rate of hydrogenation: (a) ethylenic compounds, with which the process occurs so readily that deoxygenation is scarcely noticeable; (b) simple aromatic substances, which are moderately rapidly hydrogenated (but much more slowly than the olefines), and with which removal of oxygen may cause a great decrease in the activity of small amounts of catalyst; and (c) difficultly hydrogenating substances, which can be reduced only after activation by the method of Willstätter and Jaquet (*loc. cit.*). The rate of hydrogenation is so small that deoxygenation of the platinum occurs with inconvenient rapidity. Polynuclear aromatic compounds, such as *o*-benzylbenzoic acid, *o*-naphthoylbenzoic acid, and substances which directly remove oxygen from the platinum, belong to this class.

811. Waldschmidt-Leitz and Seitz⁴ cite twenty-one references to show that the oxygen content of platinum-black determines the results obtained in hydrogenation with a platinum catalyst.

812. Skita,⁵ discussing the mechanism of catalytic hydrogenation, says Willstätter and Waldschmidt-Leitz have pointed out the necessity of priming the platinum catalyst with oxygen during the course of many hydrogenations and have advanced the hypothesis that a platinum superoxide or oxide is formed as intermediate product. This is not incompatible with Skita's observation that the activity of the catalyst produced *in situ* is superior to that of the preformed agent, since the experimental conditions did not guarantee the complete absence of oxygen. Comparative experiments with a platinum catalyst produced *in situ* do not show any difference in the rate of hydrogenation of pulegone or *as-p*-xylydine when every trace of oxygen is excluded or when special precautions to this end are not observed. The formation of a superoxide as catalyst cannot therefore be assumed in these cases. Further, if the platinum catalyst is in reality a superoxide, its oxygen must liberate iodine from potassium iodide, and hydrogenation must therefore be impossible in the presence of the salt. It is found, however, that phenol is reduced smoothly to cyclohexanol at 40° C. in the presence of potassium iodide. On the other hand, the addition of the latter completely inhibits the reduction of phenol or *as-p*-xylenol at the atmospheric temperature, whereas reaction occurs slowly but quantitatively when the mixture is heated to 50° C. At the higher temperature, therefore, it seems impossible that hydrogenation should depend on the formation of a platinum superoxide. It has not yet been elucidated whether the failure of the action at the atmospheric temperature is due to the inactivation of a platinum superoxide or to poisoning of the catalyst.

813. A meritorious contribution to this discussion is published by Zelinsky and (Mrs.) Turova-Pollak.⁶ They find that a platinum or palladium catalyst which has been inactivated by use as a hydrogenation catalyst produces carbon dioxide when oxygen is passed over it, even at room temperature. Results for nine such catalysts are reported. The curves have all the same general form: the evolution of carbon dioxide, beginning at room temperature, rises steeply to a maximum at 150°-250° C. and falls steeply again as the temperature rises to 300° C. The original activity of the catalyst is thus restored. These workers are of opinion that in every hydrogenation, at least to a small extent, profound decomposition of the reactant molecules occurs with deposit of carbon on the catalyst. This, evidently, would explain the need for and the efficacy of reactivation with oxygen. It still leaves unexplained the alleged inactivity of a new platinum catalyst formed in the absence of organic matter and devoid of oxygen. If this inactivity really exists in these conditions, we could make the Zelinsky-Pollak hypothesis cover the facts, by supposing that a brand-new catalyst is so active that immediately it comes in contact with organic matter, and before hydrogenation can take place, dehydrogenation occurs and the carbon veil forms on the catalytic surface.

⁴ *Ber.*, 1925, 58B, 563.

⁵ Skita, *Ber.*, 1922, 55, 139-143; (*J.S.C.I.*, 1922, 41, 195A).

⁶ *Ber.*, 1926, 59B, 156; *Chem. Abst.*, 1926, 20, 1599.

814. Gas Charges in Platinum Catalysts. Käß⁷ prepared platinum catalysts by electrical disintegration in various gases and in a vacuum and determined the activity by measuring the decomposition of formic acid at room temperature. Formic acid is a strong poison to platinum-black.⁸

815. The catalyst prepared in a vacuum and that prepared in an atmosphere of nitrogen were active. Those made in hydrogen, oxygen, and carbon monoxide were inactive. Platinum-black which had been exhausted in hydrogenation could be reactivated by removal of the hydrogen.

816. If the conclusions of this worker are confirmed and generalized it is conceivable that the Willstätter effect may sometimes be due to the need for removal from the catalyst of an inactivating form of hydrogen, rather than to the necessity, in catalysis, of oxygen at the catalytic surface. In this connection the overpotential phenomenon is suggestive.⁹

817. Boswell and Bayley,¹⁰ holding the view that "interior oxygen" (due to non-completion of the reduction) is vital to the maintenance of the active surface film of the catalyst, find themselves able to interpret in this sense the results of experiments on the poisoning by chlorine of platinum oxide and nickel catalysts. The catalysts were supported on asbestos. Poisoning of the catalyst is due to destruction of the active surface by chlorine, whereby the precious "interior oxygen" is exposed, forms water with the hydrogen and, until this is removed, catalysis is inhibited.

818. For nickel catalysts the necessity for the presence of oxygen seems to have been disproved by the careful work of Kelber.¹¹ This investigator has been unable to confirm the observation of Willstätter and Waldschmidt-Leitz that metallic nickel, prepared by ignition of nickel oxalate, and reducing the oxide at 350°–360° C. is incapable of accelerating hydrogenation catalytically unless previously primed with air. He has further examined the behavior of metallic nickel obtained by the reduction of basic nickel carbonate at different temperatures in the same vessel as is used for the subsequent hydrogenation experiments, thus avoiding any possible complication caused by exposing the product to air. The activity of the catalyst was examined in respect to aqueous solutions of sodium cinnamate. Metallic nickel prepared at 350°–360° C. is found to be but little inferior to that obtained at 300° C. and notably superior to that produced at 210° C. The material first described becomes completely inactive when shaken with oxygen at 18°–20° C. but if treated with hydrogen at 70°–80° becomes again active at the temperature of the laboratory. The latter phenomenon was not observed by Willstätter and Waldschmidt-Leitz since they worked at 60° C., at which temperature the catalyst commences to regain activity.¹²

819. Kelber¹³ continued to work on this subject and showed that metallic nickel deposited on a carrier, inactivated by short exposure to oxygen, was more

⁷ *Z. physik. Chem.*, 1925, **115**, 224; *Chem. Abst.*, 1925, **19**, 1804.

⁸ According to Boeseken *et al.*, *Rev. Trav. Chim. Pays-Bas*, 1916, **35**, 260.

⁹ See the discussion in Rideal and Taylor: *Catalysis in Theory and Practice*, 2d edition, pp. 425–426; 1st edition, p. 395 (over-voltage).

¹⁰ *J. Phys. Chem.*, 1925, **29**, 11.

¹¹ *Ber.*, 1921, **54**, 1701–1705; *Chem. Abst.*, 1922, **16**, 189.

¹² *J.S.C.I.*, 1921, **40**, 789A.

¹³ *Ber.*, 1924, **57B**, 136–143; *Chem. Abst.*, 1924, 2153.

readily restored than was unsupported nickel. Catalytic activity was permanently destroyed by treatment with oxygen at 60°–70°. Nickel on a carrier is much inactivated when heated with water in an atmosphere of hydrogen: this effect was not observed with unsupported nickel. Supported nickel develops maximum activity when reduced at 350°, but retains some activity when prepared at 1000°. Unsupported nickel reduced at 450° is almost inactive.

820. Working under conditions which are considered to exclude the presence of oxygen and with hydrogen which is free from any trace of the latter, the hardening of cottonseed oil has been effected in the presence of reduced nickel (from the cyanide or chloride), nickel powder, or palladized kieselguhr. It appears therefore that Willstätter's assumption of the necessity for the presence of oxygen in a nickel catalyst is unjustified.¹⁴

PLATINUM CATALYSTS

821. As a hydrogenation catalyst platinum may be used in the massive form, or as platinum sponge, or as platinum-black, or in colloidal form, or it may be introduced as an oxide.

822. Massive Platinum. Platinum in the form of wire or gauze is a catalyst of cardinal importance in modern industrial chemistry, but in the hydrogenation of organic bodies it is of little or no value.

823. Platinum Sponge. Platinum sponge is the name given to the heavy, porous form in which the metal is obtained when ammonium chlorplatinite is ignited. It is inferior in hydrogenation activity to the other platinum catalysts yet to be described and is, therefore, less used.

824. Platinum-black: Method of Preparation. A favorite method for the preparation of a platinum-black catalyst is that of Loew.¹⁵

825. Twenty-five grams of platinic chloride are dissolved in 30 cc. of water; 35 cc. of 40–50 per cent solution of formaldehyde are added; 50 g. of 50 per cent sodium hydrate solution in water are run in drop by drop, while cooling the mixture. The whole is allowed to stand for twelve hours, then filtered through a Büchner funnel and washed with water till the wash water begins to show a gray tinge. Alternatively,¹⁶ the alkaline fluid may be heated to 50° C. for fifteen minutes, then decanted, and the platinum-black washed by decantation until the washings give no reaction with silver nitrate solution. The product is dried *in vacuo* and exposed to air or to oxygen before use.

826. These directions have been changed, chiefly in regard to the temperature of precipitation and the nature of the alkali, first by Willstätter and Hart¹⁷; again, by Willstätter and Waldschmidt-Leitz¹⁸; and still again by Feulgen.¹⁹ The changes from the original directions of Loew result in the production of a more effective catalyst and eliminate a few of the experimental difficulties involved, such as that of filtration of the platinum-black. Moreover, it is reported that the platinum produced by the modified directions is more uniform in its activity as a catalyst. Even with these improvements, the production of a very active catalyst cannot be relied upon unless the directions are followed with exactness. Drying in

¹⁴ Normann, *Ber.*, 1922, **55**, 2193–2197; *J.S.C.I.*, 1922, **41**, 675A.

¹⁵ *Ber.*, 1890, **23**, 289.

¹⁶ Willstätter, 1912, *Ber.*, **45**, 1472.

¹⁷ *Ber.*, 1912, **45**, 1472.

¹⁸ *Ber.*, 1921, **54**, 113.

¹⁹ *Ber.*, 1921, **54**, 360.

a good vacuum for twenty-four to forty-eight hours is very necessary if a high activity is to be obtained.²⁰

827. As this catalyst is sensitive to traces of chlorides the elimination of these must be thorough.

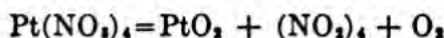
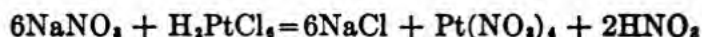
828. Paal's Method. In some cases a catalyst may be efficiently and simply produced by suspending or dissolving a platinum (or palladium) chloride in the liquid to be hydrogenated, or in a suitable solvent, and passing in hydrogen at 2-3 atmospheres' pressure and at a temperature of 80° C. Sodium carbonate should be added to neutralize the hydrochloric acid set free.

829. With olive oil rapid hydrogenation is obtained by this process, using 0.1 per cent of platinum, or even less of palladium.²¹

830. The Adams Platinum Oxide Catalyst. A platinum catalyst first described by Voorhees and Adams²² has several important advantages. The preparation is of great simplicity, the product is of uniform and of high activity. These workers, considering the two facts that platinum-black is usually active as a reducing agent only when it contains oxygen,²³ and that when platinum-black absorbs oxygen true oxides or hydroxides of platinum are formed,²⁴ concluded that platinum black from oxides of platinum should prove an excellent hydrogenation catalyst. This expectation was fulfilled and catalysts of this kind, as well as similar products containing palladium and iridium oxides, have been successfully used by Adams and his associates. The results will be dealt with under the heading of catalytic hydrogenation of organic compounds.

831. The following is a description of the preparation and method of use of this valuable catalyst:²⁵

832. Platinum Catalyst for Reductions.²⁶



833. In a porcelain casserole (a Pyrex beaker may be used) is prepared a solution of 3.5 g. (Note 1) of a commercial C.P. chloroplatinic acid (Note 2) in 10 cc. of water, and to this is added 35 g. of C.P. sodium nitrate (Note 3). The mixture is evaporated to dryness by heating gently over a Bunsen flame while stirring with a glass rod. The temperature is then raised, 350-370° C. being reached within about ten minutes. Fusion takes place, brown oxides of nitrogen are evolved, and a precipitate of brown platinum oxide gradually separates.

834. During this procedure foaming often occurs, in which case the mass is more vigorously stirred and an additional flame directed at the top of the reaction mixture. If the burner under the casserole is removed when foaming starts, the top of the fused mass solidifies and foaming

²⁰ Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397.

²¹ Paal, U. S. Pat. 1,023,753, 1912. See also U. S. Pat. 1,063,746, 1913 to Skita.

²² The Use of the Oxides of Platinum for the Catalytic Reduction of Organic Compounds, *J. Amer. Chem. Soc.*, 1922, **44**, 1397; for more detailed information on preparation of the catalyst see Adams and Shriner, *ibid.*, 1923, **45**, 2171.

²³ See numerous references in Voorhees and Adams, *loc. cit.*, especially the important paper by Willstätter and Waldschmidt-Leitz, *Ber.*, 1918, **51**, 767. Skita, *Ber.*, 1922, **55**, 139, has shown that colloidal platinum is active in the absence of oxygen. Cf. paras. 804-812.

²⁴ Wöhler, *Ber.*, 1906, **36**, 3475.

²⁵ Voorhees and Adams, *loc. cit.*, and especially Adams and Shriner, *loc. cit.*

²⁶ This description was kindly furnished by Professor Adams.

may become sufficient to carry material over the sides of the casserole. By the end of fifteen minutes, when the temperature has reached about 400° C., the evolution of gas has greatly decreased. At the end of twenty minutes the temperature should be 500–550° C. At this point the vigorous evolution of oxides of nitrogen has practically ceased and a gentle evolution of gas takes place. The temperature is held at this point (best with the full force of the burner directly on the casserole) until about thirty minutes have elapsed, when the fusion should be complete.

835. This temperature (500–550° C.) is most satisfactory for the fusion (Note 4) in order to obtain a catalyst of maximum activity and minimum lag (Note 5). The temperature indicated is generally attained by the use of one ordinary Bunsen burner turned on as high as possible; where the gas pressure is low a Meker burner may be necessary. The mass is allowed to cool and is then treated with 50 cc. of water. The brown precipitate settles to the bottom and can be washed by decantation once or twice, then filtered (preferably through a hardened filter paper on a Gooch crucible) and washed on the filter until practically free from nitrates.

836. If the fusion has been properly carried out no difficulty is encountered in this procedure; but if the temperature of fusion has not been high enough or is not maintained for a sufficiently long time the precipitate tends to become colloidal on addition of water and does not filter well; moreover, under these conditions the yield of product and its activity as a catalyst are diminished. Sometimes the precipitate becomes colloidal only when practically all of the nitrates are removed; in this case it is better to stop washing as soon as the colloid starts to form, since small traces of the salt do not affect the efficiency of the catalyst.²⁷ The filtrates should be tested for platinum and saved if any is present (Note 6).

837. The oxide is either used directly, or more generally it is dried in a desiccator and portions of the dried material weighed out for reductions. The yield is 1.57–1.65 g. (95–100 per cent of the theoretical amount). (Notes 4 and 7.)

838. The platinum catalyst, as has been found with platinum-black prepared by other methods, may sometimes be used a second, third or even more times in the reduction of certain compounds merely by reactivating (Note 8) with air or oxygen. A spent catalyst must be reworked (Note 9) along with the platinum recovered from filtrates (Note 6), filter papers (Note 10), and the casserole (Note 11).

839. In the use of platinum-oxide platinum-black for reductions, certain types of compounds require different physical conditions from others in order to obtain the best results in each case and factors such as the following must be taken into consideration: the medium in which the reduction of platinum-oxide to platinum-black occurs (Note 12), the effect of traces of inorganic salts (Note 13), the solvent employed (Note 14). Palladous-oxide palladium-black has been used for catalytic reduction, and in some cases has proved a more efficient catalyst than the platinum-oxide platinum-black, though generally this has not been found true (see para. 878).

840. Notes. 1. If a considerable quantity of platinum oxide is desired it is more satisfactory to prepare several runs of the size indicated than one large run, since spattering and the evolution of gases make large amounts inconvenient to handle. The activity of the catalyst decreases after standing for several weeks and therefore the oxide should be made up as required.

841. 2. The commercial C.P. chloroplatinic acid varies somewhat in its purity, depending on the concern from which it is purchased. In this work that from the Mallinckrodt Chemical Company, St. Louis, was used and gave very satisfactory results. Since small amounts of impurities in the catalyst are important factors in the rate of reduction of certain types of compounds, this question of impurities in the chloroplatinic acid must be taken into account (Note 13). In a large proportion of the reductions studied, platinum oxide prepared from the chloroplatinic acid mentioned gave as good results as that from spectroscopically pure chloroplatinic acid made according to the directions of Wichers.²⁸

842. 3. U.S.P. sodium nitrate could probably be used in place of the C.P. grade in most instances, but in one type of reduction at least (that of aminophenols to cyclic amino alcohols) the small amount of impurities in the U.S.P. grade affected the activity of the catalyst.

843. 4. The relation of temperature of fusion to the properties of the catalyst produced was determined by carrying out the fusion at various temperatures which were recorded by

²⁷ Garland and Reid, *J. Am. Chem. Soc.*, 1925, **47**, 2333, boiled the colloidal platinum oxide which passes the filter with sodium carbonate and obtained a precipitate of the oxide which seemed as active, catalytically, as the rest.

²⁸ *J. Am. Chem. Soc.*, 1921, **43**, 1268.

stirring continuously with a thermocouple encased in a Pyrex glass tube, and reading the temperature on a pyrometer. The product prepared at lower temperatures is usually light brown in color and has a greater tendency to become colloidal on washing. The catalyst prepared at intermediate temperatures is brown in color and at 600° has a very deep brown color. The color may vary even when the catalyst is prepared under conditions which are essentially the same, but if the temperature indicated in the procedure is used the oxide will be satisfactory.

844. The products prepared at temperatures below 450° C. and above 600° C. have a lower activity and require a greater length of time for reduction to platinum-black than those prepared at temperatures between 450° C. and 600° C.

845. If the fusion temperature is about 300° C., the yield of platinum oxide is very low, at higher temperatures the yield increases, and at temperatures of 450° C. and higher it is practically quantitative. With a proper fusion a slightly lower yield than quantitative is generally not due to non-precipitation of the platinum but to loss by spattering and to deposition of a small amount on the casserole.

846. 5. The brown oxide is a heavy granular powder which settles to the bottom of the solution in the bottle in which the reduction is carried out. It must be reduced to platinum-black before it becomes a catalyst for the reduction. When the hydrogen is admitted and the bottle shaken the brown oxide becomes black and whips up into a fine suspension. The time necessary for the change of the oxide to platinum-black is called the lag. The time of lag varies usually from several seconds to two or three minutes, depending upon the conditions under which the platinum oxide is reduced to platinum-black. In general, the lag is short provided the reduction of the oxide is carried out merely in the presence of solvent; if carried out in the presence of solvent and substance to be reduced, as is more frequently the case, the character of the substance being reduced has a considerable effect and sometimes a lag of ten to fifteen minutes occurs. In experiments where foreign salts are added as promoters or poisons the lag varies widely, though generally within a maximum of ten to fifteen minutes; exceptions occur and it was found the lag is forty to sixty minutes or more, when the platinum oxide is reduced in presence of a little sodium nitrite and an alcoholic solution of benzaldehyde. It is probable also that the temperature at which the platinum-oxide is formed from the chloroplatinic acid and the solvent present have some effect on the ease with which it is reduced to platinum-black.

847. 6. It is advisable to test for platinum in all the filtrates before discarding any of them, since there is a tendency for small amounts of platinum to remain in solution. A very satisfactory and delicate test for platinum, described by Wöhler,²⁹ consists in making the solution acid with hydrochloric acid and adding a few drops of stannous chloride. A yellow color develops when platinum is present and a brown color when it is in large amount. If any doubt exists as to whether or not the solution is yellow, it should be shaken with a small amount of ether; the yellow color concentrates in the ether layer, indicating the presence of platinum. From the sodium nitrate filtrates a large proportion of the platinum can be recovered by adding excess of formaldehyde and sodium hydroxide and heating. Upon standing, platinum-black separates and may be filtered and worked up with other platinum-black residues. The platinum which still remains in solution after this precipitation can be recovered by acidifying the solution and heating with zinc.

848. 7. Quantitative analyses show the oxide to be $\text{PtO}_2 \cdot \text{H}_2\text{O}$. It usually contains a very small amount of glaze from the platinum casserole, but this does not affect its use or activity. The oxide dissolves only slightly in hot aqua regia, even after long heating; it is insoluble in boiling concentrated nitric acid and only slightly or at least only slowly, soluble in boiling concentrated hydrochloric acid. Constant-boiling hydrobromic acid, on the other hand, dissolves it completely in the cold with the evolution of bromine and the formation of a solution of bromoplatinic acid from which the red potassium salt can be readily precipitated or the solution may be evaporated and the residue used directly in a subsequent fusion.

849. 8. The platinum-oxide platinum-black, like any other platinum-black, gradually loses its activity with use. In the reduction of certain types of compounds, notably aldehydes, the catalyst can be revived by shaking with air or oxygen for a few minutes. Frequently this must be done in order to have the reduction go to completion and often it is desirable to do so during a reduction so as to increase the rate of reaction. In other reductions such as those of pyridine salts, attempted reactivation as described above results in the complete deactivation and frequently the coagulation of the catalyst. In reducing certain substances, the catalyst tends to coagulate in lumps during the reduction, particularly toward

²⁹ *Chem. Ztg.*, 1907, **31**, 938.

the end of the reduction. In these instances reworking of catalyst is necessary (Note 9) before it can be used satisfactorily for a second run. On the other hand, in the reduction of many substances, the catalyst does not coagulate, but after the reduction is complete it gradually settles if allowed to stand, and the supernatant liquid may be decanted; when a second run is made with this catalyst it is frequently not much inferior to new catalyst and forms a fine suspension as soon as shaking is again started.

850. 9. Platinum residues may be reworked by dissolving them in aqua regia, filtering, evaporating the filtrate to dryness, taking up with a little water and fusing with sodium nitrate. If organic matter is present in the chloroplatinic acid, as is generally the case when recovered platinum is used, it will be oxidized during the fusion and, excepting in cases requiring a spectroscopically pure platinum, seems to have no deleterious effect. Repeated reworking does seem to cause an accumulation of poison in the catalyst, and under these conditions it should be purified as described by Wichers.²⁸

851. 10. There is always a certain amount of the oxide which remains sticking to the filter paper during filtration, so that these papers should be ignited and the residue added to any platinum catalyst which has already become inactive and requires redissolving and reprecipitation (Note 9).

852. 11. The thin film of oxide which remains in the casserole is dissolved by treating with a little constant-boiling hydrobromic acid (Note 7); the solution obtained may then be evaporated and the residue added to the next fusion mixture.

853. 12. In certain reductions it is an advantage to reduce the platinum-oxide to platinum-black by shaking with hydrogen in the presence of solvent only, before the substance to be reduced is added to the mixture. More often the catalyst is reduced in the presence of the substance to be reduced; with aldehydes, for example, the platinum-black is usually more finely divided and generally more active if prepared in presence of the aldehyde.

854. 13. Certain inorganic salts have the effect of promoting or retarding the action of the catalyst. Thus in the reduction of aldehydes, iron salts in mere traces have a remarkable effect in increasing the rate of reduction and in inhibiting the tendency of the catalyst to lose its activity. To a lesser extent manganese, nickel, and other salts have the same effect. On the other hand, with the majority of substances studied, the effect of these salts is to retard the action of the catalyst.

855. 14. The solvent used is an important factor influencing the rate of reduction and no generalization can be made beyond the one that alcohol, either 95 per cent or absolute, has proved to be the best solvent for most of the compounds thus far studied.

856. 15. Palladous oxide PdO, may be prepared by the fusion of palladous chloride with sodium nitrate, and is an effective catalyst in hydrogenation, the most active form being produced when the fusion temperature is 600° C.

857. A description of the apparatus will be found in the original article by Voorhees and Adams, in *Organic Syntheses VIII*, and in an article by Gough and King (see Fig. 14, page 86) in *Chemistry and Industry*, 47, 410, 1928 and in paras. 733-741 of this book.²⁰

858. **Examples of the Use of the Adams Catalyst.** In the first of these examples the catalyst is reduced in the reaction mixture: in the second, reduction takes place in the solvent only.

859. *p*-Nitroethylbenzoate to *p*-aminoethylbenzoate.

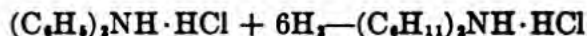


A solution of 19.5 g. (0.1 mole) of *p*-nitroethylbenzoate in 150 cc. of 95 per cent alcohol is placed in the reduction bottle and 0.2 g. of platinum oxide catalyst is added. The mixture is shaken with hydrogen until the theoretical amount has been absorbed. The time required is about seven minutes. The platinum is filtered off and the alcohol removed from the fil-

²⁰ Other articles in this field are (a) Voorhees and Adams, *J. Am. Chem. Soc.*, 1922, 44, 1397; (b) Carothers and Adams, *Ibid.*, 1923, 45, 1071; (c) Adams and Shriner, *Ibid.*, 1923, 45, 2171; (d) Kaufmann and Adams, *Ibid.*, 1923, 45, 1029; (e) Carothers and Adams, *Ibid.*, 1924, 46, 1675; (f) Shriner and Adams, *Ibid.*, 1924, 46, 1684; (g) Carothers and Adams, 1925, *Ibid.*, 47, 1047; (h) Pierce and Adams, *Ibid.*, 1925, 47, 1098; (i) Kern, Shriner and Adams, *Ibid.*, 1925, 47, 1147; (j) Heckel and Adams, *Ibid.*, 1925, 47, 1712; (k) Tuley and Adams, *Ibid.*, 1925, 47, 3061; (l) Adams and Garvey, *Ibid.*, 1926, 48, 477.

trate by distillation. The *p*-aminoethylbenzoate is recrystallized from ether and melts at 89–90° C. The yield is 15.7–16.5 g. (95–100 per cent of the theoretical amount).

860. Diphenylamine to Dicyclohexylamine.



In the reduction bottle are placed 0.25 g. of platinum oxide catalyst and 50 cc. of absolute alcohol. This mixture is shaken with hydrogen under 3 atmospheres pressure for about two minutes in order to reduce the catalyst. A solution of 20.5 g. (0.1 mole) of diphenylamine hydrochloride in 150 cc. of absolute alcohol is then added. The mixture is warmed to 50° C., the apparatus evacuated, hydrogen admitted and the reduction begun. When the pressure falls to 1.8 atmospheres, it should be restored to 3 atmospheres. When the reduction is complete (about two hours) the catalyst is filtered off, the alcohol distilled, and the amine hydrochloride treated with 50 cc. of warm water (50–60° C.). An excess of 50 per cent potassium hydroxide is added, the solution thoroughly shaken, cooled and extracted several times with ether. The ether solution is dried with stick potassium hydroxide and metallic sodium, the ether evaporated and the amine distilled under diminished pressure. The yield of dicyclohexyl amine boiling at 136–138° C. at 26 mm. is 14.8–16.2 g. (82–89 per cent of the theoretical amount).

861. Hydrogen Cyanide: Platinum Catalyst for Reduction.²¹ Barratt and Titley, for the reduction of hydrogen cyanide used a catalyst prepared by soaking blue asbestos fibre in platinum chloride solution. The resulting mass was then dried and reduced in a current of hydrogen at 150°. Catalysts containing from 0.1 to 40 per cent of platinum on the asbestos were tested. Only those preparations containing more than 10 per cent of platinum were of practical value. Those containing less platinum were not sufficiently vigorous. Such variations in the composition of the catalyst affected only the efficiency of the reduction, and not the nature of the products.

862. According to Feulgen²² the following method yields a material which does not tend to pass into colloidal solution during the process of washing and before removal of the chloride is complete.

863. A solution of chloroplatinic acid (5 g.) in water (5 cc.) is mixed with formaldehyde solution (40 per cent, 7 cc.), and sodium hydroxide (5 g.) dissolved in water (10 cc.) is gradually added. The mixture is allowed to remain for half an hour at the ordinary temperature, then heated for fifteen minutes at 55° and poured into a half-liter flask half-full of water. The flask is agitated violently for a few minutes, which causes the precipitate to settle in coarse particles, leaving an almost colorless supernatant liquor. The latter is decanted and the precipitate is washed with water strongly acidified with acetic acid, which again causes the formation of coarse particles that can now be washed as requisite without showing any tendency to pass into the colloidal state. The metal is finally filtered and dried in a vacuum over sulphuric acid. Great caution must be observed in the subsequent admission of air into the desiccator as the metal readily becomes incandescent owing to absorption of oxygen. Previous to use, it is advisable to grind and wash it once more. A very active catalyst is thus obtained.

864. Velocity of Reaction in Hydrogenation by Platinum-Black.²³ The nature of the solvent and the rapidity with which the products of reaction are removed from contact with the catalyst have an important influence on the velocity of the reaction.

²¹ *J. Chem. Soc.*, 1919, 115, 903.

²² *Ber.*, 1921, 54B, 360; *J. Chem. Soc.*, 1921, 119 and 120, ii, 266.

²³ Vavon, *Compt. rend.*, 1921, 173, 360; *J.S.C.I.*, 1921, 40, 674A.

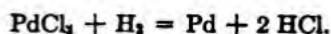
PALLADIUM CATALYSTS

865. In 1906, Fokin ²⁴ stated that he regarded palladium as the most powerful of all catalysts, having found that reduction takes place readily at 80° to 90° C., while with nickel, a temperature of 180° to 200° C. was necessary for practical hydrogenation. Fokin's experiments at that time were concerned with electrolytic reduction. By this means he reduced linseed, wood, castor and cod liver oil. He found that while palladium-black would reduce oleic acid completely to stearic acid, platinum-black under the same conditions gave only 24 per cent of stearic acid.

866. Wieland (*Ber.* 1912, **45**, 2615) considers palladium-black less sensitive to "poisons" than platinum-black, for in presence of the former a sample of benzene containing thiophene absorbed hydrogen at a noticeable rate although not so rapidly as pure benzene.

867. **Paal's Method of the Preparation and Use of Palladium and Platinum Catalysts.** Paal ²⁵ has ascertained that the reduction of the fats and fatty acids may be effected by hydrogen in presence of solid salts of the platinum metals. Both the simple salts, such as palladium protochloride (PdCl₂), platinum protochloride (PtCl₂), platinum chloride (PtCl₄), platinum hydrochloride (H₂PtCl₆), platinum sulphate and the double salts, for instance potassium chloroplatinate (K₂PtCl₆), copper platinochloride, may be used. When the double salts are used, care must be taken that no anticatalytic substances, such for instance as lead, find their way into the reduction mixture. Use may be made of salts whose acid radicals or other constituents are themselves reduced by hydrogen, for example acid platinous oxalate. In all cases the method is simple; and it is distinguished from those in which the finely divided metals are used by the omission of the preparation of the finely divided platinum metals or their protohydroxides and of the deposition on special carriers.

868. The salts in a crushed condition, preferably in the state of powder, are mixed with the fats or fatty acids to be hydrogenated; and hydrogen is allowed to act on this mixture, with stirring, at temperatures below 100° preferably under a pressure of several atmospheres. In a short time the solid reduction product of the fat or fatty acid will be obtained. All that is necessary to insure the action of the solid salts of the platinum metals is that they must be present in the solid form during the progress of the reaction. The salts may also be added to the fats in a dissolved condition (for example in aqueous solution), *the solvent being evaporated before or at the beginning of the reduction process.* A suspension of the solid salts may also be used. For example, the salts of the platinum metals may be triturated with a portion of the fat or oil that is to be reduced, the mixture being then added to the main portion of the fats or fatty acids to be reduced. Or a suspension of the salts in mineral oil may be prepared, and this mixture may be added to the substances that are to be reduced, in which case the suspensory medium may be eliminated during the process of reduction. A single salt of a platinum metal may be used, or several salts, and even several platinum metals may be mixed together; and the salts may also be used in conjunction with the platinum metals which have been deposited on carriers, devoid of anticatalytic action, such as copper, or magnesium carbonate. It is probable that, during the process, the salts of the platinum metals are split up into metal and free acid, for example:



²⁴ *Chem. Ztg.* [2], 1906, 758; [1], 1907, 324.

²⁵ U. S. Pat. 1,023,753, 1912.

869. In any case, however, the solid platinum metal salts greatly facilitate the absorption of hydrogen by fats and fatty acids. Very small quantities of the platinum-metal salts are sufficient to reduce large quantities of fat or fatty acids in presence of hydrogen. When the reduction process is completed, the platinum metals or their compounds can be easily separated from the reduced fat or fatty acid by filtration, and used again.

870. To prevent the formation of free acid, as, for example, hydrochloric acid from the chlorides of the platinum metals, in the reducing process, there is added to the powdered platinum salt a neutralizing agent, such as anhydrous soda, in sufficient quantity to combine with the liberated acid. The employment of salts of the platinum metals assists the reduction process considerably more than is done by palladium-black or platinum-black containing an amount of platinum metal equal to that in the platinum metal salts used in the present method. Thus, for example, 1.7 parts of PdCl_2 (= 1 part of Pd) in presence of hydrogen will convert 10,000 parts of fat or fatty acid into solid masses within three or four hours. If, however, the PdCl_2 be replaced by a quantity of palladium-black containing the same amount of palladium, then, with a ratio of 1 part of palladium to 10,000 parts of fat or fatty acid, these substances, according to Paal, will remain liquid, even when the palladium and hydrogen are allowed to act for twice or three times as long as with PdCl_2 .

871. Paal notes that the time required for the reduction depends on the amount of the platinum metal salt used, and on the pressure under which the hydrogen is allowed to act. By using a palladium salt as the hydrogen carrier, about 50,000 parts of fat or unsaturated fatty acid can be hydrogenated within from six to eight hours with a quantity of salt, for example, PdCl_2 , corresponding with 1 part of palladium.

872. Paal gives the following example: One million parts by weight of castor oil or oleic acid are treated with 34 parts by weight of dry palladium protochloride (= 20 parts of palladium) in the form of powder, with or without the equivalent amount of anhydrous soda; or with 140 parts by weight of dry platinum protochloride (= 100 parts of platinum) in the form of powder; or 172 parts of platinum chloride; or 230 parts of platinum hydrochloride, with or without addition of an equivalent amount of anhydrous soda. The mixture is placed in a pressure vessel, from which the air is exhausted as completely as possible, and hydrogen is then admitted into the vessel under a pressure of 2 to 3 atmospheres. The reduction mixture is kept in motion by a stirring apparatus. The vessel is heated to about 80°C , although the reduction may also be carried out at a lower temperature. The progress of the reduction and the consumption of hydrogen is revealed by the fall in pressure as indicated by the pressure gauge. When the gauge registers a low pressure, a fresh quantity of hydrogen is admitted. The completion of the reduction process can be recognized by the gas pressure remaining constant for some considerable time. When the reduction is ended, the reduction product is freed from the caalyzer in a filter press which is adapted to be heated.

873. Skita's Methods. Skita has described various modifications of a process which appears to differ from Paal's method in three points: (1) Paal uses sodium carbonate to neutralize the hydrochloric acid set free from the metallic salt, while Skita adds hydrochloric acid in some instances and omits it in others, using alkali in none. (2) Skita uses always solutions of the platinum or palladium salt. Paal usually employs the salt in the solid form: when he uses a solution, the solvent is ". . . evaporated before or at the beginning of the reduction process." (3) Paal seems to contemplate the application of his invention only to unsaturated fatty acids and fatty oils: Skita mentions, also, the hydrogenation of other organic substances, e.g., camphene. Skita³⁶ states that an unsaturated substance can be hydrogenated when there is added to it, or its solution or suspension, a small amount of palladium chloride or any other soluble salt of a platinum metal and the whole exposed to hydrogen, most advantageously under pressure. The addition of an acid is usually advantageous in this operation and hydrochloric acid is recommended; but with fatty bodies it suffices merely to add a simple aqueous solution of a compound of a metal of the

³⁶ U. S. Pat. 1,063, 746, 1913, assigned to Boehringer & Son.

platinum group. As an example, he states, that 50 g. of olive oil may be suspended in a solution containing about 0.05 g. of platinum chloride, 20 cc. of alcohol, 50 cc. of water and 8 cc. of dilute hydrochloric acid. After treatment with hydrogen at a pressure of about 4 atmospheres and at a temperature of 70° C. a solid fat results. In another example about 250 g. of castor oil is well mixed with a solution of about 0.05 g. of palladium-chloride in 5 cc. of water. The whole may then be treated at about 70° C. in an autoclave with constant stirring, with hydrogen under a pressure of 4 atmospheres. After two and one-half hours the oil will be found so far hydrogenated that it will solidify to a hard mass on cooling.³⁷

874. A method of preparing palladium catalysts is described by Sulzberger which differs scarcely at all, in principle, from the processes of Paal and Skita.

875. Sulzberger³⁸ considers that the most efficient way of intimately distributing a catalyzer is by dissolving the initial catalytic material in the body, which is to be treated, and then, should not the form, in which the material was dissolved in the body, be *per se* catalytically active, transforming it by chemical reaction or otherwise into a product of catalytical efficiency.

876. As an example, he cites the hardening of cottonseed oil with a catalytic agent belonging to the platinum group: palladium. Sulzberger notes that a palladium product of the desired quality can be obtained by treating a palladium salt, as for instance, "palladium-ammonium chloride" with sodium oleate, which resulting compound is soluble in cottonseed oil and can be used as a catalyzer of highest efficiency, as, being so finely divided in the oil, even very small quantities will give good results. The solution of this product in the oil darkens when heated, in consequence of its palladium content and such solution hardens to a product of jelly-like consistency at certain temperatures and when containing certain amounts of the palladium body. Cottonseed oil, when containing this body is readily hardened when treated with hydrogen.

877. In cases where the product, which is to act as a catalyzer, cannot be made use of in a form soluble in the body which is to be treated catalytically, the very fine distribution of the catalytic agent may be accomplished by dissolving it in a solvent, which mixes with the body to be treated, with or without precipitation. For example, the above palladium compound being soluble in ether, could be added to the cottonseed oil in such solvent.

878. Palladous Oxide-Palladium Catalyst.³⁹ Palladous oxide, prepared by a similar method to that used for platinum oxide, is an effective catalyst for hydrogenation. The activity was tested by its action on maleic acid. The best temperature for the fusion of palladous chloride with sodium nitrate was thus found to be 600°. The reduction of aldehydes is much more readily completed with palladium than with platinum and the presence of iron

³⁷ The hydrogenation of unsaturated substances is effected, according to Skita, by treatment with hydrogen in the presence of small quantities of compounds of metals of the platinum group in solution. The substances to be hydrogenated may be dissolved or suspended in a liquid (French Pat. 447,420, Aug. 20, 1912; also Brit. Pat. 28,754, Aug., 1912, and addition to the latter Patent 18,996, 1912). A solution of palladium chloride acidulated with dilute hydrochloric acid was used by Skita as a catalytic solution for the treatment of camphene. Hydrogen was used under a pressure of 1 atmosphere. The hydrogenation of olive and castor oil in this manner is described. In the addition patent Skita states that the employment of dilute acid is not always necessary since in many cases the reaction can be carried out simply by passing hydrogen through a mixture of the substances to be reduced and a solution of the salt. *J.S.C.I.*, March 15, 1913, 253.

Skita (*Chem. Zeit. Rep.* (1913), 680; Brit. Pats. 18,996, 1912, and 16,283, 1913), carries on reduction processes without the addition of any acid to a solution of a salt of the platinum group and also makes use of colloidal solutions of an hydroxide of the platinum group as a catalyst.

³⁸ U. S. Pat. 1,171,902, Feb. 15, 1916.

³⁹ Shriner and Adams, *J. Am. Chem. Soc.*, 1924, 46, 1683. Cf. paras. 831 *et seq.*

is not essential. Ferrous chloride accelerates the reduction of aromatic aldehydes which contain a free hydroxyl group, but not the reduction of the ethers derived from them; in some cases it increases the time required for reduction. The reduction with palladium differs from that with platinum in continuing until the aldehyde group has been converted into a methyl group. This further stage of reduction proceeds more slowly and in the case of benzyl alcohol is inhibited by the presence of ferrous chloride. The time of reduction is approximately proportional to the amount of the catalyst. Activation of the catalyst with oxygen accelerates the reduction of benzaldehyde, but retards the reduction of maleic acid, a similar poisoning effect being observed with platinum. The nature of the compounds to be reduced has thus an important effect, and oxygen is regarded as a promoter similar to ferrous chloride, each promoter exercising its own specific action, depending both on the catalyst and the type of compound undergoing reduction. The oxide obtained by fusing iridium chloride with sodium nitrate is not a catalyst in the reduction of aldehydes.⁴⁰

879. Sorption of Hydrogen by Palladium on Various Carriers. The absorption of hydrogen by palladium deposited on blood, beech, sponge, and bone charcoals, barium sulphate, and kieselguhr has been examined by Sabalitschka. All the carriers, freshly cleansed, were loaded with palladium to 2.5 per cent of their weight. No distinction is drawn between hydrogen simply absorbed and hydrogen taken up as palladium hydride. The carriers alone show a definite saturation capacity on repeated treatment, thus: blood charcoal, 1.35 cc. per g.; beech, 0.94; sponge, 0.84; bone, 0.72; barium sulphate, 0.00; kieselguhr, 0.26, but when the palladium is present the absorptive capacity is not constant, but rises to a maximum and then (after the third or fourth treatment, with interposed exhaustion at 300°) shows a decline. For the various systems, the figures (at this maximum) are 7.49, 2.20, 10.46, 5.27, 8.18, and 1.91, respectively. These correspond with the following when referred to the palladium present: on blood charcoal, 2924 cc. per g.; palladium, beech, 867; sponge, 4581; bone, 2167; barium sulphate, 3895; kieselguhr, 910. These results agree with such earlier ones as can be compared. The rise of the absorptive activity to a maximum and the subsequent decline are due to the gradual conversion of the palladium from the amorphous into the crystalline form.⁴¹

880. At the Vereinigte Chem. Werke at Charlottenberg, according to Colletas,⁴² hydrogenation of oils was effected at 100° C., under a pressure of 2 to 3 atmospheres by means of 0.00002 part of palladium chloride in the presence of an alkali. The loss of catalytic agent was from 5 to 7 per cent of the weight taken, which corresponds to an expense of 1.60 francs per 100 kilos of fat.

OTHER PLATINUM GROUP METALS

881. Osmium and Iridium Catalysts. Neither osmium nor iridium is of major importance as a hydrogenation catalyst. Sadikov⁴³ has used both, extended on asbestos, in various hydrogenations by Ipatiev's method. Both suffer from their high cost. Osmium is, in addition, a very disagreeable substance with which to work: the vapor of its volatile tetroxide, Os₄O₄, is irritating and its solutions produce black stains.

⁴⁰ *J. Chem. Soc.*, 1920, **126**, ii, 668.

⁴¹ *Arch. Pharm.*, 1927, **265**, 416; *Brit. Chem. Abst.*, 1927, 821A. Cf. para. 656.

⁴² *Les Matières Grasses*, 1914, **7**, 4151; *J.S.C.I.*, 1914, 972.

⁴³ See paras. 2768 and 2769, this volume.

CHAPTER IX

COLLOIDAL CATALYSTS OF PLATINUM GROUP

900. It was early recognized that fineness of division of a catalyst was favorable to high activity. It was therefore inevitable that, as soon as colloidal solutions (sols) of metals of the platinum group became available, they should be tried out as hydrogenation catalysts.

901. Preparation of Hydrosols of the Platinum Group. Platinum was first prepared in the form of a colloidal dispersion in water by Bredig.¹ He struck an arc between platinum electrodes under pure water.

902. Colloidal solutions (hydrosols) of metals of this group, as well as of gold, silver, copper, lead, iron, zinc, tin, nickel, aluminum, bismuth, antimony and cadmium, have been prepared with great ease by an electrical disintegration method, using a high-frequency alternating arc, the leads to which were taken from two points on the inductance of the oscillatory circuit of a Poulsen arc as used in wireless telegraphy. By varying the conditions it was possible to pass currents of from 0.14 to 15 amperes and E.M.F. of 480 to 4080 volts, and colloidal solutions showing a wide range of colors were thus obtained from a number of the metals.^{1a}

903. Protective Colloids. Hydrosols, such as are produced by Bredig's and by chemical reduction methods are unstable. Furthermore, they are not reversible, that is, if the sol is evaporated to dryness, the metal will not again go into solution on treating it with water. Stable reversible sols (colloidal solutions) may be obtained by the addition of suitable colloidal substances, which are known as protective colloids. Usually such substances are organic (e.g., Paal's sodium lysalbate, gum arabic), but Schwerin² uses colloidal silicic acid.

904. Paal's Lysalbinic Acid. To prepare lysalbinic acid Paal dissolves 15 parts of sodium hydrate in 500 of water, adds 100 of egg albumin and warms on the water-bath. When solution is nearly complete the liquid is acidified with sulphuric acid and the precipitate filtered off. The filtrate is neutralized with sodium hydrate, evaporated to a small bulk and again acidified and filtered. The filtrate is dialyzed to separate sodium sulphate. The remaining sulphate ions are removed by the addition, to the warm contents of the dialyzer, of a solution of baryta, followed by filtration. This filtrate is evaporated on the water-bath and several volumes of alcohol added. White flakes are precipitated. The dried product is a white powder, soluble in water and nearly insoluble in alcohol. To this Paal has given the name lysalbinic acid.³

¹ *Zeit. physik. Chem.*, 1901, **37**, 1-323.

^{1a} Morris-Airey and Long. *Proc. Univ. Durham Phil. Soc.* 1912-1913, **5**, 68; *J.S.C.I.* 1913, 1015.

² U. S. Pat. 1,119,647, 1914.

³ Paal and Amberger, *Ber.*, 1902, **35**, 2195.

905. Colloidal Platinum with Sodium Lysalbate. One gram of lysalbinic acid, dissolved in 30 cc. of water, is rendered slightly alkaline with soda, 2 g. of platinum chloride dissolved in a little water are added and then a slight excess of hydrazine hydrate. The solution darkens and a gas is evolved: after five hours it is dialyzed to remove electrolytes, evaporated on the water-bath and the drying finished in a vacuum. Brilliant black scales are obtained which dissolve in water to a black solution. This is colloidal platinum with sodium lysalbate as a protective colloid.

906. Such a colloidal solution is stable. The method of preparation illustrates its reversibility. A similar product made with sodium protalbate and containing about 60 per cent of colloidal palladium has been an article of commerce.⁴

907. Gum Arabic as Protective Colloid. Colloidal solutions prepared with lysalbate, or the similar protalbate, suffer from the disadvantage that they are coagulated by acids. This is a serious handicap in the treatment of organic compounds, many of which undergo hydrogenation best in acetic acid solution. Hydrosols having gum arabic as the protective colloid are free from this drawback. Their preparation is also easier than that of the lysalbate type.

908. The simplest way of using gum arabic is to extemporize, so to speak, the hydrosol in the presence of the gum and of the substance to be hydrogenated. To a solution of the substrate, a solution is added containing 1 per cent each of platinum (or palladium) chloride and of gum arabic: hydrogen is then passed at atmospheric or at slightly higher pressure. If the substrate (substance to be hydrogenated) is an aldehyde or a ketone the metal will be reduced in a colloidal form. In the case of other substrates a trace of previously prepared colloidal metal must be added (Skita's inoculation or "germ" method), otherwise the metal will separate in a granular inactive form.⁵

909. In the absence of a substrate, this germ method affords a convenient way of making a stable stock hydrosol.

910. Kelber and Schwarz's Protective Colloid. Another protective colloid which can be used for the hydrogenation of compounds in glacial acetic acid solution is described by Kelber and Schwarz.⁶ This is the product obtained by acting on gluten with glacial acetic acid.

911. To 16 g. of the gluten-acetic acid solution, containing about 50 per cent gluten, add 4 g. palladium chloride dissolved in a little water. To this solution add a small amount of ammonia, then hydrazine hydrate, drop by drop. Froth is formed and a gas given off. When reduction is complete dialyze till the outside water gives no chloride reaction. Evaporate the colloidal solution cautiously, finishing the drying in a vacuum. The product is easily soluble in water and in acetic acid; the solution is not coagulated by dilute mineral acids.

912. "Galactose" Protective Colloid. "Galactose," resulting from protracted boiling of aqueous glue solutions, is advanced by Classen as a protective colloid for finely divided metals, a salt of the metal being reduced in the presence of this agent.⁷

913. Silicic Acid as Protective Colloid. Schwerin⁸ uses silicic acid in making stable colloidal solutions of metals.

914. A solution of silicic acid containing about 2.5 per cent of the acid is mixed with a diluted solution of a gold or silver salt and the metal is reduced by a reducing agent suitable for separating it in the colloidal form. If, for instance, hydrazin hydrate is the reducing agent a completely clear brown silver sol, or deep blue gold sol, is obtained.

⁴ Prepared by Kalle & Co., Biebrich am/R. See Paal and Hartman, *Ber.*, 1910, **43**, 248-249.

⁵ Skita and Meyer, *Ber.*, 1912, **45**, 2579, 3589; D.R.P. 230,724.

⁶ *Ber.*, 1912, **45**, 1946.

⁷ *Zeitsch. angew. Chem., Referat*, 1915, 58; Ger. Pat. 281,305, 1913.

⁸ U. S. Pat. 1,119,647, 1914.

915. Colloidal palladium with titanium dioxide as protective colloid may be prepared as follows: a solution of titanium trichloride is nearly neutralized with sodium acetate, then boiled and, after cooling, added to a 1 per cent solution of palladium dichloride ($\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$). The production is relatively insensitive to acids.⁹

916. Stable colloidal platinum is prepared by Kiyoshi Shigena by reduction of PtCl_4 in the presence of sodium citrate. An excess of the latter decreases the stability.¹⁰

917. Colloidal Rhodium. Colloidal rhodium suitable for use in experiments on catalysis was made as follows: To a slightly alkaline solution of sodium chlororhodite, a solution of sodium protalbinat was added, and the rhodium reduced by means of formaldehyde at a temperature of 40°C . The solution was purified by prolonged dialysis. Such solutions are clear and have remained unaltered for over two years. They may be evaporated *in vacuo*, giving very stable glistening, black plates containing 33 per cent rhodium. On twenty-four hours' contact with hydrogen, these solutions absorb a volume of gas 2509 to 2728 times the volume of rhodium contained. At 12° – 14° they absorb 346 volumes of carbon dioxide per unit volume of rhodium, and at 60° , 1820 volumes, a fact which indicates that the carbon dioxide absorbed is probably in chemical combination with the rhodium.¹¹

918. Catalysis with Colloidal Palladium at Room Temperature.¹² Bourguet's catalyst for hydrogenation in the cold was made by reducing sodium chloropalladite with hydrazine hydrate in the presence of starch as a protective colloid. The catalytic hydrogenation of acetylenic hydrocarbons was studied. The reaction was found to be selective, yielding reductions only to ethylenic hydrocarbons. In an additional communication (*Bull. Soc. Chim.*, 1927, **43**, 231) Bourguet mentions that rice starch and other small grain starches are not so successful as protective colloids as are the wheat and potato starches.

919. Hydroxide Catalysts of the Platinum Group. These are prepared by boiling a solution of the metallic salt (palladium chloride or potassium chlorplatinate) with the theoretical amount of sodium carbonate in decinormal solution and a little gum arabic. The product is dialyzed to eliminate chloride and carbonate and evaporated cautiously, finishing in a vacuum. The resulting solid is insoluble in water but dissolves on addition of a trace of alkali. Such a solution, carefully neutralized, dialyzed and evaporated yields black scales readily soluble in water.

920. These hydroxide colloidal solutions are efficient hydrogenation catalysts, and can be used in acid media.¹³

921. Commenting on British Patent No. 18,642 to the Vereinigte Chemische Werke, Fokin states that in 1906 he published a communication on the reduction power of platinum hydroxide and, in fact, had made application for patent in Russia in April, 1909. In 1910 he published a further communication in which the theory of the process and the function of the three factors, namely: the hydrogen atom, the hydroxyl group, and the double bond were discussed. Fokin observed that complex compounds of platinum were formed which are organosols. These possess a surface of "unlimited" area, which accelerate the reaction in the highest degree. Later, in a publication on the preparation of isomers of oleic acid, the procedure was more fully detailed by Fokin and methods of determining the hydrogen number were described, in which platinum oxide was used as the catalytic agent.¹⁴

⁹ Gutbier and Weithase, *Z. anorg. Chem.*, 1928, **169**, 264; *Brit. Chem. Abst.*, 1928, 359A.

¹⁰ *Repts. Imp. Ind. Research Inst. Osaka*, 1927, **8**, No. 2, 1; *Chem. Abst.*, 1927, **21**, 2829.

¹¹ Zenghelis and Papaconstantinos. *Compt. rend.*, 1920, **170**, 1058; *Chem. Abst.*, 1920, 3348.

¹² *Bull. soc. chim.*, 1927, **41**, 1443; *Chem. Abst.*, 1928, **22**, 2099.

¹³ Skita and Meyer, *loc. cit.*

¹⁴ *Zeit. analyt. chemie*, **48**, 337 and *J. Russ. chem. Gesell.*, 1908, 700.

922. Lehmann carries out the hydrogenation of oils or unsaturated fatty acids by passing hydrogen through oil containing a small amount of osmium tetroxide, while the oil is being heated. Osmium dioxide forms from the tetroxide, producing a colloidal solution which can be removed by animal charcoal. In one experiment 10 g. olive oil with 0.05 g. osmium tetroxide produced in one and one-half hours a fat of melting-point 39°C . It is not necessary to use hydrogen under pressure.¹⁵

923. Normann and Schick hold that, contrary to the views of Lehmann, osmium metal and not the dioxide, is responsible for the catalytic action noted in fat hardening.¹⁶

924. Colloidal hydroxides of osmium and ruthenium and the colloidal metals themselves may be prepared according to Kalle und Co. A.-G.¹⁷ by means of a protective colloid. The tetroxide of osmium or of ruthenium is mixed with the protective colloid, such as sodium protalbate or lysalbate, and with alcohol, and the mixture evaporated carefully to dryness. The solid colloidal hydroxide thus obtained may be reduced to the colloidal metal by means of hydrogen at a low temperature. The advantage of this modification is found in avoiding the admixture of salts and alkalies and in the fact that dialysis is not necessary. The preparation in detail is as follows: One part sodium protalbate is dissolved in 200 to 300 parts water and then 1.34 parts osmium tetroxide in about 60 volumes cold alcohol is added. The mixture is then either evaporated to dryness *in vacuo*, or else gently heated on the water-bath to remove most of the solvent and finally dried *in vacuo*. The osmium tetroxide is reduced by the alcohol to the tetrahydroxide $\text{Os}(\text{OH})_4$. If evaporation is effected *in pleno*, ammonia must be added from time to time in order to prevent reoxidation of the hydroxide to the volatile oxide. If the process is applied to ruthenium tetroxide, the alcohol must be added to the solution of the protalbate or lysalbate of sodium, and the tetroxide, dissolved in water is allowed to flow gradually into the solution with stirring. Ruthenium chloride, Ru_2Cl_3 , or the potassium salt of the acid may be used as the initial material, which is first converted by treatment in a current of chlorine, in the presence of water with heating, into the tetroxide. If the osmium or ruthenium hydroxides are to be converted into the corresponding colloidal metals, the solid products are carefully powdered and treated in a tube freed from air by carbon dioxide with hydrogen at 30° to 40° , obtaining thereby colloidal Os or Ru. If the colloidal tetrahydroxides are to be obtained in dilute aqueous solution, a smaller amount of stabilizer will be sufficient.¹⁸

925. Organosols of the Platinum Group. Paul and Amberger¹⁹ prepare products of a greasy consistency containing inorganic metal colloids of the platinum group, consisting in incorporating solutions of the divalent salts of the metals of the platinum group with bodies maintaining colloids in the colloidal state (protecting colloids) especially with wool fat or the alcohols obtainable therefrom by saponification, and adding a carbonate of an alkali to form the colloidal lower hydroxides of the metals employed. They note that preparations containing combinations of the divalent salts of the metals of the platinum group in a colloidal condition can be obtained, if, instead of the alkali carbonates used above, the alkali salts of certain weak organic acids are selected, for instance, the salts of the higher, saturated, or unsaturated, fatty acids (soaps). In this way there are produced in the presence of solutions of the metal salts, for

¹⁵ *Arch. Pharm.*, 1913, 152; *Seifen. Ztg.*, 1913, 418.

¹⁶ *Seifen. Ztg.*, 1914, 111; *Arch. Pharm.*, 1914.

¹⁷ Ger. Pat. 280,365, July 30, 1913. Addition to Ger. Pat. 248,525; *J.S.C.I.*, 1915, 492 and 1912, 952.

¹⁸ *Chem. Abst.*, 1915, 1378; *Zeitsch. angew. Chem.*, *Referat*, 1915, 22.

¹⁹ U. S. Pat. 1,077,891, 1913.

instance, of divalent palladium, or platinum, triturated with wool fat, products which contain the corresponding palladium, or platinum, salts dissolved in colloidal form in the wool fat.

926. If, according to Paal and Amberger, wool fat be impregnated with a concentrated aqueous solution of palladous chloride (PdCl_2) and the mass be then triturated with the equivalent quantity of potassium oleate in concentrated aqueous solution, the salts mutually decompose with formation of potassium chloride and palladous oleate which remains dissolved in colloidal form in the wool fat. As the palladous chloride is difficultly soluble in pure water but readily in hydrochloric acid it is dissolved in the latter and the acid is neutralized before triturating the liquid with wool fat by means of an amount of sodium carbonate equivalent to the hydrochloric acid used. The neutral PdCl_2 then remains dissolved in the liquid.

927. In order to obtain a preparation containing about 25 per cent colloidal palladous oleate 0.85 part of palladous chloride $\text{PdCl}_2 = 0.5$ part of palladium is dissolved with the application of heat in 0.45 part of fuming hydrochloric acid (38 per cent HCl) and 2 parts of water, and the hydrochloric acid is neutralized by the addition of 0.3 part of anhydrous soda either solid or dissolved in 0.7 part of water. The solution of PdCl_2 thus obtained is then triturated intimately in small portions with 9.5 parts of wool fat softened at a gentle heat. Into the body thus obtained are then stirred, also in small portions, 3.5 parts of potassium oleate dissolved in 15 parts of water. The formation of the palladium oleate is detected by the fact that the greasy mass colored red-brown by the palladous chloride becomes, on being triturated with the potassium oleate, first yellow-brown, then gray-brown and, after being allowed to stand some considerable time, black-brown. To purify the product it may be either treated repeatedly with hot water at from 50° to 60° C., and the mass exposed in *vacuo* at from 40° to 50° C., for the purpose of removing the water; or the original product may be dissolved in from 5 to 6 times its volume of petroleum ether of low boiling-point, the greater part of the by-products remaining undissolved and the red-brown liquid organosol being dried with calcium chloride or dehydrated sodium sulphate. In this case a further part of the by-products separates along with the water. The petroleum ether is then distilled off from the liquid freed from the drying agent. The colloidal palladium oleate can be enriched in the "ointment" body by solution in petroleum ether and precipitation with alcohol. A product is thus obtained containing about 70 per cent of colloidal palladium oleate, which like the 25 per cent preparation, is absorbed as organosol by all organic substances dissolving wool fat. Instead of a palladous salt, a platinum or other salt of the platinum group can be used, for instance, the salt of divalent platinum resulting from the reduction of the platinum-chloride-hydrochloric acid with sulphur dioxide. Wool fat impregnated with platinum salt, when acted on by an aqueous solution of potassium oleate, forms a colloidal platinum oleate $(\text{C}_{18}\text{H}_{33}\text{O}_2)_2\text{Pt}$. A mixture of the wool fat alcohols obtained from wool fat by saponification can be used in the same manner as wool fat. The wool fat alcohols are in their properties very similar to the wool fat itself and the mixture of alcohols obtained therefrom by saponification presents a still greater affinity for water than wool fat. The wool fat alcohols have a more solid consistency than the wool fat.

928. Amberger (*Kolloid-Zeit.* (1913), 13, 310) has prepared organosols of palladium, platinum, palladous hydroxide, palladium oleate and platinum hydroxide. In the preparation of the metallic organosols, hydrazine hydrate was used as a reducing agent. The palladium organosols (8 : 9 to 16 per cent palladium) had pronounced catalytic activity; small quantities dissolved in fatty oils were capable of transferring hydrogen to the unsaturated glycerides of the oil, with the formation of hardened oils. The platinum organosols contained 8.14 to 18.4 per cent platinum. The hydroxide organosols were prepared by the interaction of the corresponding chlorides and sodium carbonate and the palladium oleate organosols from the chloride and potassium oleate in presence of wool fat. (*J.S.C.I.* 1914, 41.)

929. Osmium Organosols. By the method previously applied to platinum and palladium, Amberger prepared organosols of osmium. The method is interesting and suggestive, though osmium is of minor value as a hydrogenation catalyst.²⁰

930. Two parts of osmium tetroxide are dissolved in 7 parts dilute caustic soda and alcohol added till sodium osmate is formed. This is gradually stirred into 13 parts of warm wool fat, intimately mixed, then hydrazine hydrate is added slowly; the emulsion swells and takes on a metallic gray color and on standing twenty-four hours becomes black. Another

²⁰ See para. 881.

warming and the addition of more hydrazine hydrate are necessary for complete reduction. To remove by-products the mass may be dissolved in petroleum ether, washed, dried and the ether distilled off. There results a brown-black salve, easily soluble in organic liquids which dissolve wool fat, giving transparent, brownish-black liquids. For analysis this salve is dissolved in petroleum ether, precipitated by more than an equal volume of alcohol and osmium determined in the dry precipitate by the method of Knotte. The osmium content is about 7.9 per cent. This contains oxides of osmium as well as metallic osmium. In order to reduce the colloidal oxides the original emulsion, after reduction with hydrazine hydrate, is dissolved in petroleum ether and precipitated by alcohol; nearly all the osmium precipitates in combination with a large proportion of the wool fat. The coagulum is washed free from alkali, dried, powdered and then reduced with dry hydrogen first in the cold then at 30° to 50°. This gives a stable organosol, easily soluble in liquids which dissolve wool fat. The osmium content is 20.9 per cent. If instead of reducing the sodium osmate wool fat emulsion with hydrazine hydrate, sulphuric acid is added, an organosol of osmium dioxide is formed, one preparation of which gave 0.53 per cent osmium dioxide. By dissolving in petroleum ether and precipitating with alcohol, then washing, the concentration may be raised to an osmium dioxide content of 24.5 per cent.²¹

931. In his dissertation entitled "Über katalytische Hydrierungen organischer Verbindungen mit kolloidem Palladium und Platin," Karlsruhe, 1912, Meyer draws the following conclusions: Methods of reduction depending on the use of a solution of palladous chloride and gum arabic in water-alcohol mixture, forming colloidal palladium with hydrogen, do not progress satisfactorily unless bodies are present which are capable of forming addition compounds with palladous chloride. The action of hydrogen on a hot solution of palladium chloride and a protective colloid gives rise to a colloidal solution of palladium. From colloidal palladium or platinum solutions using gum arabic or gelatine as a protective colloid, the corresponding reversible metal colloid is obtained. With the aid of gum arabic or gelatine as a protective colloid it is possible to obtain permanent colloidal solutions of palladium and platinum hydroxide. By careful evaporation and drying of these colloidal solutions solid products are obtained which may be brought again into colloidal solution by peptization. Stable colloid solutions of palladium may be advantageously obtained by the reduction of dialyzed colloid palladous hydroxide solutions. For the production of a colloidal solution of platinum it is recommended that reduction of chlorplatinic acid by hydrogen in the presence of a protective colloid be employed, in which case the mixture should first be inoculated with small amounts of colloidal platinum or palladium. Colloidal solutions of platinum and palladium with gum arabic or gelatine as a protective colloid are well adapted to the hydrogenation of olefine bodies. The hydrogenation of aromatic bodies with colloidal metallic platinum is possible only in strong acetic acid solutions. The hydrogenation of aromatic bodies is carried out more easily with platinum than with palladium. While gum arabic is suitable for use as a protective colloid with platinum or palladium in the hydrogenation of certain organic bodies, it is found that gelatine under some conditions acts as a catalyzer poison. Vulcanized rubber also affects the activity of the catalyzer. The inoculation method for the production of colloidal solutions of platinum affords a convenient laboratory procedure for the hydrogenation of aromatic bodies as the formation of the colloidal solution and the process of hydrogenation follow one another quickly. The hydrogenation of aromatic bodies using colloidal platinum as a catalyzer progresses three or four times quicker than when platinum-black is employed. See also *J.S.C.I.*, 1913, 46, and *Ber.*, 1912, 45, 3379.

932. Meyer reports an experiment on the hydrogenation of olive oil with a colloidal palladium hydroxide solution containing 0.2 g. palladium and 0.34 g. gum arabic in 100 cc. Two volumes of olive oil to 1 volume of the colloidal solution were heated and agitated in an autoclave at a temperature of 70° to 80° C. under a hydrogen pressure of 6 atmospheres. Hydrogen was added to replace that absorbed. After one-half hour no further absorption of hydrogen could be noted, but the agitation was continued for two hours. The fat was then separated from the colloidal solution and boiled with water. A solid fatty product was obtained.

933. Hydrogenation involving the use of colloidal palladium differs from some other processes of catalytic reduction in that the reaction has not been observed to proceed in the absence of water nor if the proportion of water in the

²¹ *Kolloid-Zeit.*, 1915, 17, 47-51; *Chem. Abst.*, 1915, 3159.

reaction mixture be too small. For instance, in the case of cottonseed oil, a portion of this material showed no absorption of hydrogen on being shaken with a small quantity of powdered colloidal palladium. The same result was obtained whether the oil was suspended in 95 per cent alcohol or dissolved in acetone. On adding 15 to 20 per cent of water to the acetone solution, however, reduction took place at a fairly rapid rate.²²

934. In order to prevent the aggregation of a colloidal compound such as palladium hydrate and the like, it has been suggested²³ to use a solid fat in which the colloidal particles are fixed so that the organosol is rendered stable. The use of a solid fat of low iodine number such as is prepared by hydrogenation and preferably one which has been completely saturated with hydrogen enables such metallic organosol, especially metal catalyzers, to be preserved over an indefinite period.

935. Retarding Action of Protective Colloids. Groh²⁴ has measured the retarding effect exercised by protective colloids on the decomposition of hydrogen peroxide by colloidal platinum.

936. The following values show the times required by colloidal platinum to effect 50 per cent decomposition of the peroxide without and in the presence of protective colloids. Without a protective colloid twenty minutes, 0.1 per cent gelatin two hundred and sixty-five minutes, 0.1 per cent gum arabic eighty-six minutes, 0.1 per cent dextrin sixty-six minutes, 0.01 per cent gelatin one hundred and fifty minutes, 0.01 per cent gum arabic thirty-nine minutes, 0.01 per cent dextrin twenty-eight minutes, 0.001 per cent gelatin one hundred and three minutes, 0.001 per cent gum arabic twenty-one minutes, 0.001 per cent dextrin twenty-three minutes, 0.0001 per cent gelatin seventy-one minutes.²⁵

NOBLE METAL CATALYSTS ON CARRIERS

937. Influence of Carriers on Noble Metal Catalysts. The influence of various carriers on noble metal hydrogenation catalysts has been studied quantitatively by Karl²⁶ by Paal and Karl²⁷ (palladium) and by Paal and Windisch²⁸ (platinum). The work reported in paragraphs 656 and 879 should be noted.

938. Karl has studied with considerable care and in a quantitative way the action of palladium supported on various bodies. He found that palladium precipitated on finely divided nickel or magnesium proved effective catalytically, while if precipitated on lead, aluminum, iron, or zinc, little or no hydrogenation was effected, owing to the anticatalytic action of these metals. While metallic zinc is anticatalytic, zinc oxide and carbonate have no such effect. In these investigations Karl worked principally with fish, cotton and castor oil and oleic acid.

939. Paal and Karl tested palladium on various carriers as catalytic material for hardening fats and have found that the oxides, hydroxides and carbonates of lead, cadmium, zinc, aluminum and iron have an anti-catalytic action similar to the metals which they contain. The corresponding compounds of nickel and cobalt, and also magnesium oxide, were investigated. These carriers were coated with palladium by mixing with a solution of palladium chloride in a weak aqueous solution of hydrochloric acid at room temperature, or slightly warmed. Palladium hydroxide was thus precipitated and reduction was obtained by treatment of the powder, which was first moistened with ether, to the action of hydrogen at room

²² Albright, *J. Amer. Chem. Soc.*, **1914**, 2188.

²³ Kalle & Co., Ger. Pat. 284,319, March 1, 1914. See also Ger. Pats. 268,311 and 289,620, *Chem. Abs.*, 1916, 2618.

²⁴ *Zeit. physik. Chem.*, **88**, 414.

²⁵ *Chem. Abst.*, 1915, 7.

²⁶ *Inaug. Dissert.*, Erlangen, 1911.

²⁷ *Ber.*, 1913, 3069; *Chem. Ztg. Rep.*, 1913, 642.

²⁸ *Ber.*, 1913, 4010.

temperature. The catalyzer was mixed with fatty material without permitting contact with the air and reduction was carried out in an agitator in an atmosphere of hydrogen. Magnesium oxide did not retard the catalytic action of palladium. In fact, the reduction process appeared to be somewhat increased by the presence of this material.

940. Paal and Windisch carried on similar experiments with platinum. Metal powders of various sorts were purified with alcohol and ether and then platinized by shaking with a solution of chlorplatinic acid. Metallic oxides and carbonates were platinized by the action of sodium carbonate and hydrazine hydrate on a solution of chlorplatinic acid containing the oxide or carbonate in suspension. These products as catalyzers in the hydrogenation of cottonseed oil were found to have differing degrees of catalytic action, and only nickel and magnesium had no influence on the activity of the platinum. The platinum was much less active in the presence of aluminum, cobalt and bismuth, and was rendered completely inactive by iron, copper, zinc, silver, tin and lead. Of the oxides and carbonates examined, only the magnesium compounds were without influence.

941. Since platinum deposited in the interior of a porous support is less useful than when it is on the external surface von Artner²⁹ has devised a method to limit the deposition to the outside of the support. He impregnates the support with a volatile liquid before treating it with the platinum solution. Afterwards the liquid may be removed by evaporation. The liquid may contain formaldehyde or other reducing agent.

942. Excellent catalysts have been prepared by Reyerson by reducing upon the disperse surfaces of silica gel microscopic layers of copper, silver, gold, platinum and palladium. This was accomplished by allowing the gel to adsorb hydrogen, which was then able to reduce to the metallic state the metal ions from solution of the salts of the metals noted. This method of preparation insures maximum metal surface for catalytic reactions.

943. The catalysts were studied for the simple hydrogenation of ethylene. The palladium catalyst was able to accomplish 90 per cent hydrogenation at zero degrees and one passage of gas through the catalyst. The platinum catalyst caused about 60 per cent conversion under the same conditions, while copper was only 5 per cent effective. A nickel catalyst prepared under modified conditions was also found to be very effective in the reduction of ethylene. It was also used in the reduction of phenol and aniline and found to be very efficient. The platinum catalyst showed remarkable activity in the oxidation of hydrogen at low temperatures and also in the oxidation of ethylene. Formaldehyde was produced under certain conditions. An attempt was also made to reduce water gas. In two instances tests for formaldehyde were obtained when palladium was used as a catalyst.³⁰

944. **Platinum Group Metals on Carbon.** Colloidal metals³¹ of the platinum group are deposited in a "nascent" state on carbon; gum, dextrin, gelatin, etc., being used as protective colloids. The by-products are filtered off, the colloid is dried and then heated for a short time. The catalyst so prepared is said to be remarkable for its durability.

945. A platinum-carbon catalyst is the subject of a patent to Ellis.³² The platinum and carbon (charcoal) are in admixture. Great care to exclude oxygen is enjoined.

946. By the addition of animal charcoal Mannich and Thiele find the absorption capacity of palladium for hydrogen is greatly increased, and the mixture absorbs much more gas than the total quantity absorbed by the separate constituents. A catalyst which rapidly effects the complete hydrogenation of fats is prepared by shaking powdered, ignited animal charcoal with palladium chloride

²⁹ Swiss Pat. 127,224, Feb. 14, 1927; *Chem. Abst.*, 1929, **23**, 1227. See para. 661.

³⁰ *Chem. Met. Eng.*, **32**, 637 (1925). See paras. 676 to 679.

³¹ E. Merck Chem. Fab., Ger. Pat. 342,094, June 21, 1919; *J.S.C.I.*, 1922, **41**, 89A.

³² U. S. Pat. 1,174,245, Mar. 7, 1916.

(preferably 2 per cent) solution and hydrogen until no more gas is absorbed. The powder is then washed and dried and can be kept unaltered. It can be used in conjunction with any solvent and, after hydrogenation, is completely separated by simple filtration, without leaving any trace of metal in the fat. In these respects it is superior to colloidal palladium preparations. Even by the use of 1 part of palladium (distributed over animal charcoal) to 150,000 parts of peanut oil the hardening can be effected in one operation.³³

947. On account of the high price of osmium and ruthenium or their compounds they are used by the Badische Co.³⁴ for catalytic purposes on special carriers, in order to secure the greatest possible surface action. This is effected by solutions of their compounds such as alkali osmate and alkali ruthenate. The resulting contact masses can be employed either directly or after previous special treatment, such as heating, action of alkalies, acids, or reducing agents, etc. Asbestos, oxide of magnesium or aluminum, pumice stone, meerschaum, clay, cement, kieselguhr, metals, coal, etc., find application as carriers. For example, granulated meerschaum is saturated with a solution of potassium osmate in dilute caustic potash, and the water evaporated *in vacuo*, so that 2 to 5 per cent of osmate remains upon the carrier.

948. By the method of Schwarzman³⁵ a precipitated sesquioxide is treated with a soluble salt of a platinum group metal, such as palladium, until a certain amount of active compound is deposited; the treated sesquioxide is then dried at a comparatively low temperature, best after thorough washing; the hydrated sesquioxide being advantageously formed under conditions permitting adsorption or absorption of colloid organic matter, such as keratin dissolved in caustic alkali.

949. The sesquioxide may be ferric hydrate, chromium hydrate or aluminum hydrate, the latter giving best results. Other hydrated non-basic or slightly acid oxides, such as hydrated tin oxide, titanous acid, tungstic acid, etc., may be used but have no particular advantage over the sesquioxides. Hydrated oxides of the type of cobalt oxide, nickel oxide and zinc oxide, for general hydrogenation work are stated to be far inferior to the sesquioxides. Palladium is the best metal of the platinum group to use for the purpose of hydrogenating, although platinum compounds may be used for this purpose, and for oxidizing are even better. Osmium, ruthenium, and rhodium also may be used.

950. The hydrated sesquioxides although not active as hydrogenating agents *per se*, according to Schwarzman appear to heighten the activity of palladium in some degree as "co-catalysts." This is said to be particularly true with palladium hydroxide distributed through hydrated alumina. Anhydrous alumina, as a carrier, he states affects the activity of palladium but little if at all. The hydrated oxides are all readily soluble in dilute acids which is convenient in regenerating the catalyst.

951. According to a formula by Schwarzman, 342 parts of aluminum sulphate, $Al_2(SO_4)_3$, are dissolved in 3400 parts of water and the temperature is adjusted to about 170° F. A solution of 240 parts of commercial caustic soda or the equivalent amount of carbonate, in 1000 parts of water at about the same temperature, is then added. The addition of soda results in the precipitation of hydrated alumina. This precipitate is washed until all the soluble salts have been removed. The hydrate so obtained is next treated to incorporate palladium. For this purpose 0.312 part of palladium chloride is dissolved in 100 parts of water and the hydrated alumina treated with this solution. The mixture then is brought to a boil, filtered and the solid material washed. This treatment leaves the alumina charged with merely the quantity of palladium it will absorb. The material after washing is dried at a moderate temperature. A high temperature is apt to cause dehydration of the palladium oxide, and of the alumina as well, to an undesirable extent. A drying temperature of about 170° is best. Using the amounts of materials indicated, there will be obtained about 156 parts of a fine-grained brown powder containing approximately 0.2 per cent palladium. Generally most of this palladium exists in the catalyst in the form of a hydrate.

³³ *Ber. Deutschen pharm. Ges.*, 1916, 26, 36-48; *J.S.C.I.*, 1916, 548.

³⁴ Ger. Pat. 292,242, Dec. 27, 1912.

³⁵ U. S. Pat. 1,111,502, Sept. 22, 1914.

952. A more active catalyst in a somewhat different physical form is obtained by using a little keratin or other organic colloid dissolved in the caustic soda used for forming the hydrated alumina. Wool is very well suited. The same reagents in the same proportions may be used together in the manner indicated above with the exception, that about 5 parts of wool, are previously dissolved in the caustic soda solution. The final material obtained is more fluffy and bulky than where the wool is omitted. This fluffy bulky catalyst is kept in suspension in the oil with particular readiness.

953. Schwarzman states that since palladium oxide does not form soaps with fatty acids, it may be employed in hydrogenating free oily and fatty acids and that as alumina is insoluble in fatty acids, the palladium carried by this sesquioxide makes a particularly good catalyst for this purpose.

954. An interesting form of catalyst investigated by Mittasch, Schneider and Morawitz³⁶ contains the elements of a metal of the platinum group and an aluminate silicate, and can be obtained by taking an aluminate silicate containing water, such as a natural or artificial zeolite, and replacing a part or the whole of its content of alkali metal or alkaline earth metal, by the platinum metal.

955. The product obtained can be subjected to further treatment. For instance, it may be heated and reduced, and this reduction is desirable if the catalytic agent is to be employed for the hydrogenation of organic compounds. After such reduction, the catalytic agent contains a platinum metal in a metallic form and also the elements of an aluminate silicate.

956. The introduction of the platinum metal into the silicate can be effected by digesting the alkali metal aluminate silicate with a solution of a platinum metal salt. Or, the zeolite as obtained (or after being gently heated, so that some of the water is driven off) may be soaked in a solution of a platinum metal salt, so that the platinum metal salt enters the zeolite, and some replacement of the alkali metal or alkaline earth metal by a platinum metal takes place, although the alkali remains in the mass.

957. *Example:* Digest 100 parts of the artificial zeolite, sodium aluminate silicate (such as the ordinary commercial granular sodium permutite found on the market) with a weak hydrochloric acid solution containing one-tenth of a part, to half a part, of palladium subchloride, either at ordinary temperature, or while warming, until the solution is decolorized. If the catalytic agent is to be used for hydrogenation purposes, wash the mass well and dry it and reduce with hydrogen at from 150° to 200° C., or with formaldehyde at a lower temperature. The catalytic agent which is obtained can be used (either directly, or after pulverization) for the hydrogenation or dehydrogenation of organic compounds, and, when liquids are treated, these can with advantage be allowed to trickle over the catalytic agent. Instead of sodium permutite, other aluminate silicates containing an easily replaceable base, or more than one easily replaceable base, can be employed, for instance, natural zeolites can be used, such as analcime, natrolite, chabasite. In a similar manner, other platinum metal zeolites can be prepared, for instance, those of platinum itself and of rhodium, iridium, ruthenium and osmium. A platinum zeolite can be obtained by heating an artificial zeolite until more or less of the water has been driven off, and then soaking it in a solution of platinum hydrochloride, drying and heating, whereupon, any soluble salts, such as sodium chloride can be removed by washing or digesting. An osmium zeolite can be prepared by soaking a zeolite in a solution of potassium osmate, and heating. The artificial or natural zeolite can first be converted into ammonium zeolite, and this either directly or after heating can be converted into osmium zeolite, by treatment with potassium osmate.³⁷

958. Vereinigte Chemische Werke A.-G.³⁸ make use of a palladium catalyzer precipitated on an indifferent body as a carrier and recommend as carriers finely

³⁶ U. S. Pat. 1,215,396, Feb. 13, 1917; cf. Brit. Pat. 1,358, Jan. 27, 1915.

³⁷ Artificial zeolites are put on the market under the name of permutite, and are described in British Patent No. 23,706/12 and also in the article "On Artificial Zeolites" by Siedler, on page 262 of the report of Section 2 of the Seventh International Congress of Applied Chemistry held in London in 1909.

³⁸ Ger. Pat. 236,488, Aug. 6, 1910; also Brit. Pat. 18,642, 1911.

divided metals which do not have anti-catalytic properties, also metal oxides and carbonates. Under these circumstances it is stated that 1 part of palladium is sufficient to convert in a few hours 100,000 parts of oily material to a firm mass. They recommend the use of a hydrogen pressure of 2 to 3 atmospheres and a temperature somewhat above the solidification point of the saturated fat. They caution against arsenic, hydrogen phosphide and sulphide, liquid hydrocarbons and carbon disulphide, chloroform, acetone and free mineral acids as being destructive to the activity of the catalyzer.

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CHAPTER X

NICKEL CATALYSTS: GENERAL ¹

1000. The generalization of the use of nickel and its congeners as hydrogenation catalysts is due to Sabatier and his collaborators. Nickel, alone or with a promoter, is by far the most important catalytic agent used in both experimental and industrial hydrogenation at the present day. It is inexpensive, robust and highly active.

1001. An examination of patents relating to the hydrogenation industry shows that more than one-third of them relate to the preparation and use of nickel catalysts, while at least half of the remainder deal with other aspects of hydrogenation with this metal.

1002. A German Patent, 139,457, of July 26, 1901, to J. B. Senderens, is probably the first patent record having to do with the reduction of organic bodies by hydrogen in the presence of nickel catalysts. This patent is for the production of aniline from nitrobenzol and involves passing the latter body in the form of a vapor over heated nickel, copper, cobalt, iron or palladium in the presence of hydrogen. The hydrogen may be in the pure state or in the form of water-gas.

1003. From a lengthy paper published by Sabatier and Senderens ² the following notes on nickel catalysts have been abstracted. Access of air to the catalysts oxidizes it and destroys or diminishes its activity. To prepare catalytic material one should use an oxide quite free of chlorine or sulphur. Good results are obtained by dissolving the metal in pure nitric acid and forming the oxide by calcination at a low red heat. Reduction of the oxide should be with pure hydrogen, free from chlorine or sulphur. Reduction should take place at a low temperature, always below a red heat, or the catalyst will not be efficient.

1004. Nickel reduced at a red heat has practically no activity. At 300° C. it gives a *very* active material if used *immediately*. It is better, however, to employ a temperature of 350° C. Copper is best treated at 300° C., while cobalt ³ requires 400° C. Iron is difficult to reduce. At 450° C. some six or seven hours are required to completely transform the oxide into the metal. Nickel and copper are actually reduced near 200° C., so even if some oxidation of the catalyst

¹ Much of the matter in Chapters X and XI is applicable, with obvious modification, to other base metals.

² *Ann. de Chim. et de Phys.*, 1905 (4), 319.

³ The reduction of cobalt oxides by hydrogen and carbon monoxide at different temperatures is described by Kalmus. (*Jour. Ind. Eng. Chem.* 1914, 112-114.) For some metals the minimum temperature of reduction is lower with carbon monoxide than with hydrogen (Fay and Seeker, *J. Am. Chem. Soc.*, 1903, 641).

were taking place, because of the presence of oxygen in the hydrogen gas, immediate reduction would occur thereafter.

1005. The hydrogen employed is dried with sulphuric acid, is then passed through a tube of Jena glass filled with copper turnings maintained at a low red heat and finally goes through a long tube filled with fragments of caustic potash.

1006. The catalyst should be prepared in the tube in which the material to be hydrogenated is treated.

For high temperatures a copper tube heated in a bath of equal parts of sodium and potassium nitrate (which melts at 225° C.) may be used.

1007. With regard to the life of the catalytic material the investigators state that there are three periods noticeable.

1. A short period when the catalyst is becoming "accustomed" to the atmosphere of hydrogen and the body to be treated.

2. A period of normal activity.

3. A period of decline.⁴

1008. The second or normal period is generally very long, if no trace of bodies capable of altering the surface of the metal is present. For example, with a nickel catalyst good results were secured for one month in the transformation of benzene into cyclohexane. The operation was interrupted each night and resumed the next morning. The slight oxidation over night did no harm as the oxide was reduced again the next day at the temperature of working, which was 180° C.

1009. If in the hydrogen there is a trace of certain bodies, the action of the catalyst is rapidly suppressed. Even tiny traces of chlorine, bromine, iodine or sulphur paralyze the nickel. Nickel obtained from oxide carrying a little chlorine is usually devoid of activity. Nickel from oxide containing a trace of sulphur is likewise inefficient. The presence in the hydrogen of even faint traces of hydrochloric acid, hydrogen sulphide or selenium compounds produces the same disastrous effects. Traces of bromine in some phenol which was used paralyzed the nickel. The same thing happened with benzol containing this compound.

1010. Catalysts finally lose their efficiency either by traces of poisons or by a deposit of tarry or carbonaceous material on the catalyzer particles. On dissolving spent nickel in hydrochloric acid a fetid gas is evolved and brown carbonaceous material is deposited.

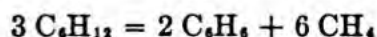
1011. It is of historic interest to note that at the date of their memoir (1905) Sabatier and Senderens lay much stress on the necessity of avoiding the deposit of *liquid* on the catalyst, stating that the lower limit of temperature is imposed by the necessity of maintaining the substrate (substance submitted to hydrogenation) in a state of vapor. This may seem surprising in view of the enormous amount of catalytic hydrogenation of liquid oils with nickel catalysts which is

⁴ These periods are similar to those noted in the case of ferments. Ferments are catalysts elaborated by living organisms and catalysts of other origin have been called artificial ferments.

practiced to-day. It must, however, be remembered that these workers were dealing with bodies which are volatilized at temperatures below those at which the hydrogenation activity of nickel is manifested. The arrest of the reaction which they reported, and which they regarded as due to covering of the catalyst surface with liquid, was directly caused by the temperature being allowed to fall below that of catalytic activity.

1012. Nevertheless, so heavily did the authority of Sabatier weigh on the pioneers of catalytic hydrogenation of fatty oils that the earliest methods proposed dealt with the fatty acids, which are readily volatilized, and not, as in later practice, with their glycerides, the natural oils, which cannot be volatilized.⁵

1013. Too high a temperature of operation may cause a reversal, with dehydrogenation and decomposition. Benzene becomes cyclohexane at temperatures up to 240° C., but at 300° C. the cyclohexane gives benzene and methane:



1014. Some peculiarities of catalytic nickel have been recorded by Senderens and Aboulenc.⁶ These investigators state that the temperature at which nickel oxide is reduced by hydrogen is found to depend on the mode of preparation and treatment of the oxide used, there being also a considerable difference between the temperature at which reduction commences and that at which it is complete. Complete reduction is not effected below 300° C., but the mixture of metal and oxide thus obtained is more active than the metal prepared by total reduction at a higher temperature, the activity of reduced nickel being diminished by heating to a comparatively high temperature, although, at the same time, its catalytic properties are rendered more permanent. Pyrophoric nickel, when heated in the air, furnishes an oxide which is reducible at a comparatively low temperature, and reduced nickel of impaired activity may be restored, therefore, by oxidizing it and again reducing.⁷

1015. According to Moissan the protoxide of nickel in hydrogen at 230° to 240° C. blackens and reduces, giving a body pyrophoric at ordinary temperature. Müller states the protoxide of nickel at 210° to 214° C. in hydrogen loses 11 to 14 per cent of oxygen, apparently giving nickelous oxide which corresponds to a loss of 10.7 per cent oxygen. At 270° C. it passes into the metallic state. For hydrogenation the anhydrous or hydrated oxide of nickel supported on pumice is reduced at 270° to 280° (Brunel); 280° (Leroux); 255° to 260° (Godchot); 245° to 250° (Darzens).

⁵ Except in the vacuum of the cathode rays (Kraft).

⁶ *Bull. Soc. Chim.* 1912, II, 641.

⁷ This may be correlated with a similar phenomenon reported by Taylor (*Trans. Amer. Electrochemical Soc.*, 1904, 6, II, 187). If hydrogen be passed over the copper oxide wire of commerce, rapid reduction begins in the neighborhood of 300° C. If the copper so formed be oxidized at a somewhat lower temperature it will be found that subsequent rapid reduction will occur at a lower temperature than in the first reduction. This process of oxidation can be repeated to such a degree that the wire becomes sufficiently reactive to be reduced or oxidized at 100°. This progressive increase of reactivity was found to be accompanied by a visible physical change comparable with that undergone by platinum used in ammonia oxidation.

1016. Senderens and Aboulenc, however, after a protracted investigation, record results which in brief are as follows: (a) Anhydrous nickel oxide: This oxide becomes green a little above 200° C. in presence of hydrogen, but the reduction commences only at about 300° C. and is slow at 330° C. It goes on much faster at 380° C. up to two-thirds the amount of water which should be evolved. There reduction stops. To get complete reduction the temperature has to be raised to 420° C. The nickel obtained is pyrophoric. It serves very well for the hydrogenation of carbon monoxide, carbon dioxide, benzene and toluene, but does not work well with the phenols.

(b) Nickel oxide obtained by calcination: This shows a great resistance to reduction. It is necessary to raise the temperature to 420° C. to obtain two-thirds of the water of theory and to a red heat to secure complete reduction. Heated to this last-named temperature the product is inactive even with carbon monoxide which is very easily hydrogenated. It is pyrophoric, however. The efficiency of nickel as a catalyzer does not depend on any pyrophoric property. Nonpyrophoric nickel has been prepared which is a good catalyzer. Reduction of the oxide (b) at 420° C. gives about one-third oxide with two-thirds metal. This mixture is active and pyrophoric. It easily converts water gas into methane.

(c) Hydrate of nickel: Introducing hydrate, prepared in the laboratory, into the tube used for reduction, the dehydration was very slight at 200° C., while at 230° C. reduction took place and at 270° C. dehydration and reduction progressed, but rather slowly. In another experiment the same "hydrate" was reduced after gently heating in a crucible to remove the water. The reduction presented the same variations commencing about 230° C. and progressing very gently up to 270° C. at which point water was given off regularly for six hours in an amount corresponding to one-third the total expected from the reduction of the oxide. At 300° C. two-thirds of the water was collected and at 320° C., the remainder was obtained after treatment for several hours. Another hydrate of nickel furnished by a chemical supply house was more difficult to reduce, not giving off as much water as the preceding at temperatures 20° to 30° higher.

1017. Anhydrous oxides and hydrates of nickel cannot be completely reduced to the metal at 300° C., but a mixture of the metal and oxide results. It is nevertheless true that such mixtures are more active than if complete reduction with corresponding elevation of the temperature had taken place.

1018. Two stages of oxidation, derived from the same pyrophoric nickel of which in one case the reduction was arrested at 250° C. when one-half the oxide remained, and in the other case the material was heated up progressively to 350° C. to give total reduction, were tested. The latter hydrogenated xylenol normally, while the former gave a hydrocarbon. To evade this destructive action in a number of cases the investigators heated the nickel after reduction to a higher temperature to diminish its activity and conserve its life as a catalyzer.

1019. Sabatier and Espil have found nickel reduced from the oxide at temperatures above 350° C. is capable of hydrogenating the benzene ring. Frequent assertions have previously been made to the contrary. Sabatier and Espil find that nickel reduced at 500° and maintained for eight hours at 500° to 700° in an atmosphere of hydrogen is still active in this respect. When heated to 750° it would no longer act to carry hydrogen to the benzene ring although it was still capable of effecting the reduction of nitro bodies.⁸

1020. Sabatier states that nickel reduced from the hydroxide at 250° C. is not only unduly sensitive, but is difficult to control. Applied to phenol it tends to produce cyclohexane instead of cyclohexanol.⁹ With this goes the statement of Taylor:¹⁰ "Heat treatment of an active catalyst preparation is now our standard method of preparing catalysts with controlled adsorptive capacity or catalytic activity."

⁸ *Bull. Soc. Chim.*, 1914, **15**, 779.

⁹ Sabatier (tr. Reid), *Catalysis in Organic Chemistry*, 56.

¹⁰ *Colloid Symposium Monograph*, 1923, 104.

1021. Influence of Reduction Temperature and Time on Catalytic Activity. Yamaguti ¹¹ has examined the effect of reduction temperatures from 300° to 800° C. on the activity of a nickel catalyst for the *decomposition of methane* at 850° C. The most active catalyst was that prepared at 600° C. Yamaguti then reduced nickel at 600° C. for eight to thirty hours. The best catalyst was that which had been reduced at 600° C. for eighteen hours. It contained 79.5 per cent free metal. These results have, evidently, no direct application to hydrogenation catalysts for ordinary working temperatures, but are special to the class of dehydrogenation catalysis with which they were obtained.

1022. Benton and Emmett ¹² have investigated the kinetics of the reduction of nickelous and ferric oxides in hydrogen. They find that the reduction of the nickel oxide is autocatalytic, but that this is not the case with ferric oxide. This lines up with the work of Pease and Taylor ¹³ on copper oxide. The explanation offered is that oxides which form solid solutions with their metals will not be autocatalytic in reduction, while those which do not form such solid solutions will show autocatalysis. Iron falls in the first class, nickel and copper in the second. See graph, Fig. 14a, page 126.

1023. In the case of nickel oxide it was found that the higher the temperature of preparation, the higher the temperature necessary to obtain a useful rate of reduction, and the less the autocatalytic effect.

Emmett confirms observations of other workers ¹⁴ that supports and promoters sometimes retard reduction or require a higher temperature.

1024. Gallo ¹⁵ has also examined the course of the reduction of nickel and cobalt oxides by hydrogen. The reduction of nickel "sesquioxide" ¹⁶ in dry hydrogen begins at 92°–95° C. In the presence of water vapor of pressure 92 mm. reduction commences at a higher temperature and proceeds more slowly. With cobalt sesquioxide reduction is first detectable at 80°–85° C. and complete reduction requires several hours at high temperatures.

1025. Comparison of Catalysts from Different Raw Materials. Kahlenberg and Pi ¹⁷ have made a comparative study of catalysts reduced from different compounds, chiefly nickel compounds. These catalysts have been tested in the hydrogenation of various oils and have been found to exhibit important differences in their behavior under catalytic hydrogenation.

¹¹ *Bull. Chem. Soc. Japan*, 1917, **2**, 289.

¹² *J. Am. Chem. Soc.*, 1924, **46**, 2728. A more generalized treatment of the subject of oxide reduction was given by Emmett at 51st Genl. Meeting—*Amer. Electrochem. Soc.*, 1927.

¹³ *J. Am. Chem. Soc.*, 1921, **43**, 2179.

¹⁴ Taylor and Gauger, *J. Am. Chem. Soc.*, 1923, **45**, 920 (nickel on diatomite); Taylor and Russell, *J. Phys. Chem.*, 1925, **29**, 1325 (nickel with thoria promoter). In order to obtain catalysts active at low temperatures the temperature of reduction must be correspondingly low. This is secured by reduction in presence of a catalyst (French pat. 650,592, Mar. 8, 1928 to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1929, **23**, 3315).

¹⁵ *Annali Chim. Appl.*, 1927, **17**, 535, 544.

¹⁶ This would be Ni_2O_3 . "No trivalent salts [of nickel] are known, and the trivalent hydroxide which is frequently mentioned in the literature appears to be the hydrated dioxide." Latimer and Hildebrand: *Reference Book of Inorganic Chemistry*, Macmillan, New York, 1929. Cf. LeBlanc and Sachse, *J. anorg. allgem. Chem.*, 1927, **168**, 15; *Chem. Abst.*, 1928, **22**, 3107.

¹⁷ *J. Phys. Chem.*, 1923, **28**, 59–70.

1026. The hydrogenation of cottonseed oil was carried out with catalysts obtained by reduction in a current of hydrogen of: nickel oxide, nickel molybdate, nickel tungstate, tungsten oxide, nickel silicate, nickel borate, iron silicate, a mixture of iron and nickel silicates, nickel glycinate, nickel tyrosinate, thorium stearate, thorium silicate, nickel chromate, nickel manganate, and cobalt silicate. The hydrogenation of soya-bean oil was conducted with catalysts made from nickel silicate, borate, molybdate, tungstate, chromate, and manganate. Olive oil, corn oil, neat's-foot oil, and a fish oil, and oleic acid and the fatty acids from cottonseed, soya-bean, fish, and neat's-foot oils were also hydrogenated with the nickel silicate catalyst. Nickel silicate proved to be the most active catalyst among those tested in the hydrogenation of cottonseed oil. The best temperature for the reduction of this catalyst is 290°–300° and for the hydrogenation of the oils 180°–200°. Nickel tungstate was found to be efficient in the hydrogenation of cottonseed oil, but to require rather a high temperature for its reduction. Iron retards the catalytic activity of nickel when both these metals are present in the catalyst. Hydrogenation of soya-bean oil is stated to be difficult, but may be accomplished by means of nickel chromate or manganate, the iodine value of the oil being reduced to about half its original value. The hydrogenation of free fatty acids is reported to be more readily accomplished than that of the corresponding glycerides. The case of neat's-foot oil is an example.¹⁸

1027. That the activity of a nickel catalyst is much influenced by the conditions of preparation and especially by the temperature to which it has been subjected is now a commonplace. The matter has been quantitatively investigated chiefly by Taylor and associates, by Armstrong and Hilditch in England and by Kelber in Germany.

1028. An important paper on this subject was published by Gauger and Taylor,¹⁹ from which the following excerpts are taken:

THE ADSORPTION OF GASES BY NICKEL
GAS VOLUMES ADSORBED AT 760 MM. GAS PRESSURE

Sample	Support	Wt. Gms.	Wt. Ni Gms.	Gas	Cc. (0-760 mm.) adsorbed by sample				Cc. (0-760 mm.) adsorbed per vol. of Ni			
					25°	184°	218°	305°	25°	184°	218°	305°
(A)	None	15.0	15.0	H ₂	8.7	7.9	7.0	5.4	5.2	4.7	4.2	3.2
(B)	Diat. earth	11.0	1.1	H ₂	6.30	6.15	5.65	...	50.7	49.8	46.3	...
(C)	Diat. earth	10.4	1.0	H ₂	5.70	5.60	5.35	...	50.7	49.8	47.2	...
				CO ₂	...	1.8	16.0
(E)	Diatomite	10.0	1.0	H ₂	4.8	42.7
					175°	200°	225°	250°	175°	200°	225°	250°
(D)	Diatomite	7.5	0.75	H ₂	3.8	3.9	...	3.5	46.3	45.4	...	42.1
				CO ₂	1.3	1.2	1.1	.9	15.1	14.2	13.4	11.8
				CO	5.25	50.4

(A) Oxide from nitrate, calcined at 300°, reduced in stream of pure, dry hydrogen at 300°.

(B) One gram nickel supported on 10 g. diatomaceous earth. Diatomaceous earth soaked in nickel nitrate solution, dried, calcined at 300°; reduced by more than one week's treatment with pure, dry hydrogen at 350°.

(C) As (B) except that it was reduced for forty minutes at 500°.

(D) Nickel 10 per cent on Nonpareil diatomite brick (8- to 10-mesh). Reduced at 300° from low temperature calcined oxide.

(E) Like (D) except calcination at 400° and reduction at 300°–500° for twenty-five minutes. All these catalysts were of a high degree of activity.

¹⁸ *Brit. Chem. Abst.*, 1924, 184B. [These findings are not wholly in accord with the usual expectations in such cases. Well-refined soya-bean oil is easily hydrogenated by any active nickel catalyst, while, on the other hand, free fatty acids generally are far more obstinate with respect to hydrogen addition than the corresponding glycerides.—AUTHOR.]

¹⁹ *J. Am. Chem. Soc.*, 1923, 44, 920.

1029. Comparison of the results for nickel (A) with those of Taylor and Burns illustrates the fact that the previous history of the sample may have no little effect upon the capacity which it exhibits for adsorbing hydrogen. The discrepancies in the literature may well be due in part to the treatment accorded the sample before adsorption measurements were made. These have been considered by Taylor and Burns.²⁰ In this connection, it is to be noted that the values given in the tables represent a steady state of adsorptive capacity. The first experiment after the reduction of sample (A) showed an adsorption of 10.4 cc. at 25°. The second was at 80.5° with a value of 9.3 cc. The value of 8.7 cc. at 25° is the mean of a number of values ranging from 8.5 cc. to 8.9 cc. obtained after numerous experiments at different temperatures. As a check, a run was made at this temperature after the final run at 305° and the value of 8.5 cc. was obtained, which is evidence of a steady adsorptive capacity.

1030. The effect of supporting the metal on an inert material was to increase its capacity for adsorbing hydrogen almost ten-fold, which may be explained on the basis of increased effective surface. An additional advantage of using a support material such as diatomaceous earth lies in the fact that the catalyst may be subjected to more severe heating in the reduction process without destruction of its adsorbing power. Sample (C) was maintained at 500° for forty minutes during the course of reduction, yet showed practically the same adsorbing power as did sample (B) which was reduced at 350°. Sample (E) supported on diatomite brick was reduced at 500° for ten minutes and showed an adsorptive capacity only slightly less than that of sample (D) on diatomite brick reduced at 300°. These results are in good agreement with those of Kelber and of Armstrong and Hilditch²¹ who showed that nickel hydroxide precipitated on diatomaceous earth and reduced at 500° is an extremely active catalyst. Taylor and Burns²² have shown that heating the nickel to 600°–700° decreases the adsorption between 80 and 97 per cent, and Sabatier states that nickel reduced at 700° is practically inert as a catalyst. Armstrong and Hilditch have shown that ignition of an *unsupported* catalyst at 500° in hydrogen is sufficient to impair seriously its catalytic activity. This influence of the support is of considerable importance since complete reduction cannot be attained at a temperature below 420° (Senderens and Aboulenc, para. 1016).

1031. It is also worthy of note that the oxide when supported on diatomaceous earth cannot be reduced at a temperature below 350° excepting extremely slowly, whereas unsupported nickel is rapidly reduced at this temperature. It would appear that the reduction of nickel oxide is an interface phenomenon, as has been shown to be the case for the reduction of copper oxide by hydrogen.²³

1032. The investigation by Taylor and Burns to which reference has been made, showed, in addition to other things not immediately relevant, that methods of preparation which produce active catalysts also produce metals with

²⁰ *J. Amer. Chem. Soc.*, 1921, **43**, 1277.

²¹ Kelber, *Ber.*, 1916, **49**, 55, 1868. Armstrong and Hilditch, *Proc. Roy. Soc.*, 1921, **99A**, 490.

²² *J. Amer. Chem. Soc.*, 1921, **43**, 1277.

²³ Pease and Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2188.

high adsorptive capacity for gases whose reaction they catalyze. High adsorptive capacity is associated with low minimum temperatures for catalysis. The fact that the temperature of maximum adsorption is often lower than that of maximum catalytic activity may be due to the higher temperature causing a freer evaporation of reactants and resultant from the catalytic surface.

1033. The paper by Armstrong and Hilditch²⁴ is the sixth of a long and important series on various problems of catalytic actions at solid surfaces. It deals with surface area and specific nature of a catalyst as two independent factors controlling the resultant activity. The apparent volume, pyrophoric character, and catalytic activity of nickel obtained by the reduction of (a) powdered fused nickel oxide, (b) precipitated hydroxide and (c) hydroxide precipitated on kieselguhr were compared. The pyrophoric character of the nickel is in no way related to its catalytic activity. The behaviors of the oxides and hydroxides of nickel during reduction at various temperatures show that changes in rate of reduction are due to physical condition and not to the formation of sub-oxides. A preparation of nickel oxide and kieselguhr in such proportions that nickel constituted 14.62 per cent of the dry mixture was separated into parts. Different parts were reduced more or less completely. The reduced nickel varied from 13 to 98 per cent. No increase of catalytic activity appeared as a result of further reduction after 60 per cent of the nickel was reduced. Pure nickel oxide sometimes suffers a decrease in catalytic activity as it is brought from partial to complete reduction. However, such decrease of activity is accompanied by a decrease in *volume* and consequently of surface. These phenomena indicate that in such cases it is the surface area of nickel, and not the presence of any other catalyst, which determines the catalytic activity.²⁵

1034. Results obtained by Thomas²⁶ with nickel hydroxide on an equal weight of kieselguhr at various temperatures of reduction are shown in the following table, the activity obtained with a catalyst reduced at 250° C. being taken as unity. The activities of the reduced catalyst were determined by ascertaining the time required to reduce the iodine value of olive oil by one-half, using 0.25 per cent of nickel at 180° C. for the hydrogenation. The inverse ratio of the times is a measure of the comparative activities. In each case the reduction was effected until not more than 5 per cent of unchanged oxide

Temperature of reduction	Time required for half transformation of olive oil (T)	Activity of the catalyst $\left(\frac{K}{T}\right)$
250° C.	60 minutes	1.0
350° C.	51 minutes	1.18
500° C.	48 minutes	1.25
650° C.	254 minutes	0.23
750° C.	24 hours	Negligible

²⁴ *Loc. cit.*

²⁵ *Chem. Abst.*, 1922, 16, 188.

²⁶ *J.S.C.I.*, 1923, 42, 3, 21T-26T.

remained. At 250° C. this operation required twelve hours, while at the other temperatures it was effected in about one hour.

When preparing a nickel catalyst by reduction with hydrogen, therefore, in order to secure maximum activity, the temperature of reduction should be about 300° C. in the case of an unsupported catalyst, and between 350° C. and 500° C. with nickel supported on kieselguhr.

1035. Some interesting observations have been made by Kelber²⁷ on the catalytic hydrogenation of organic compounds with non-noble metals at room temperature.

The catalytic action of the reduced nickel metals is stated to be greatly increased if the compounds employed (best the basic carbonates) are first deposited on a suitable carrier (infusorial earth, Florida clay, the various commercial hydrosilicates of aluminum and magnesium, blood charcoal, the decolorizing charcoal of the ferrocyanide manufacture, linden charcoal, etc.). The reduction is best effected in aqueous or aqueous-alcoholic solutions. In alcohol, benzol, acetone, ethyl ether and ethyl acetate it is slower; the addition of a little water, especially with ethyl ether and ethyl acetate, greatly accelerates it; in acetic acid it is rapid with nickel reduced at 310°. Chloroform is not suitable. To get an approximate comparison of the catalytic action of reduced non-noble metals with that of colloidal palladium, the detonating gas catalysis was carried out; Kelber and Schwartz palladium preparation²⁸ was used; 0.2 g. This (= 0.0344 g. Pd) showed an activity which at first was less than that of 0.5 g. nickel (α) (from the basic carbonate) reduced on 4.5 g. of an inorganic carrier in hydrogen at 450°, although it gradually increased as compared with the activity of the nickel and finally surpassed it. A nickel prepared at 310° or 450° without a carrier gave a negative result. In the reduction of 0.75 g. cinnamic acid in 50 per cent alcohol, however, preparation (α) and 3.0 g. nickel reduced at 450° have about the same effect as 0.5 g. reduced at 310°, while 0.5 g. reduced at 450° without a carrier is enormously less effective than preparation (α); in an aqueous alcoholic solution of sodium cinnamate the nickel reduced at 310° has the same effect as an equal weight of nickel reduced at 450° on a carrier. Cobalt may be used instead of nickel but the reduction is slower. Other substances reduced in this way were sodium phenyl propionate, quinine hydrochloride, diphenyldiacetylene, sodium "cotton oleate."

1036. Brochet²⁹ discusses the use of nickel as a catalyst in organic chemistry. Pyrophoric nickel prepared for use as a catalyst loses its characteristic property if placed in water or an organic fluid, without much detriment to its catalytic powers. If these are diminished to any extent by this treatment they may be restored to full activity by reheating the metal in a current of hydrogen. The density of catalytic nickel appears to have little relation to its activity³⁰ and the total available surface is not the only factor to be considered. The physico-chemical condition of the surface may have considerable influence; further, the extent of the occlusion of hydrogen by the metal appears to be uncertain as the measurements hitherto published are not consistent with each other.

SUMMARY

1037. The preceding paragraphs set out the results reported by different workers on the properties of nickel catalysts prepared under varying conditions. It was, therefore, not possible to make the arrangement strictly according to subject matters. For this reason the following summary of important results is inserted.

²⁷ *Ber.*, 1916, **49**, 55-63; *Chem. Abst.*, 1916, 897.

²⁸ *Chem. Abst.*, 1912, **6**, 2757.

²⁹ *Compt. rend.*, 1922, **175**, 1073; *J.S.C.I.*, 1923, **42**, 104A.

³⁰ *Cf.*, Bedford and Erdmann, *Fr. Pat.* 451,155; *J.S.C.I.*, 1913, 602.

1038. Raw Material. This should preferably be nickel nitrate free from arsenic, chlorine and sulphur. A preferred material results from the solution in pure nitric acid of the nickel cubes produced by the Mond carbonyl process.

1039. Ellis has shown that (using the precipitation method) pure nickel sulphate is an unexceptionable raw material. This is in agreement with his observation that traces of sulphuric acid carried over by hydrogen from a wash-bottle into a mixture of oil and nickel have no deleterious effect on the course of the reaction or on the life of the catalyst.

1040. Preparation of Material for Reduction. This may be done by calcining the nitrate with free access of air, or by precipitating the hydroxide or carbonate and thoroughly washing and drying the precipitate.

1041. Oxide from Nitrate. This is made by calcining in a crucible at about 300° C. The resulting oxide is very resistant to reduction: at 420° two-thirds reduction and high activity (Senderens and Aboulenc); at 300° a highly active catalyst is obtained (Gauger and Taylor).

1042. Hydrate, etc. Less resistant to reduction: two-thirds reduction at 300°, complete reduction at 320° (Sabatier and Senderens).

1043. Temperature of Reduction. For unsupported nickel this should be 320°–350°: lower temperatures tend to produce catalysts too susceptible to poisons; higher temperatures impair the activity; nickel reduced at 700° is almost inactive. The temperature for satisfactory reduction may be progressively reduced by alternate oxidation and reduction.

1044. Effect of Carrier. Nickel supported on an inert carrier requires a higher temperature for reduction, reduction being inappreciable below 350° and extremely slow at that temperature. Supported nickel tolerates higher temperatures without loss of catalytic activity: at 500° reduction is rapid and the product is of high activity. For a given weight of metal the hydrogen adsorption capacity may be increased tenfold in some cases by extending the catalyst on an inert carrier. Such supported catalysts are generally more robust.

1045. Degree of Reduction. Incompletely reduced oxide is more active than pure metal, not because of the presence of oxide, but because the higher temperature required for complete reduction impairs the activity (Senderens and Aboulenc), owing to shrinkage of the catalyst (Armstrong and Hilditch, arguing from direct measurements and, by inference, from the measurements of Gauger and Taylor).

1046. Effect of Oxygen. The weight of evidence is against the belief held by some that the presence of oxygen is necessary for hydrogenation with nickel catalyst (Kelber: Normann).

1047. Pyrophoric properties are not essential to catalytic activity.

CATALYSTS FROM MASSIVE METAL

1048. One of the main objects aimed at by those who have proposed catalysts made from massive nickel metal is the avoidance of chemical precipitation methods. Another is the simplification of regeneration of the used catalyst.

1049. Bolton ³¹ treats nickel wool with nitric acid so as to attack the surface only. The nitrate is converted to oxide and the latter reduced by hydrogen. The reaction chamber is packed with this catalyst. Regeneration is effected *in situ* by removing adherent nickel soap with hot oil and the oil with a suitable solvent. The catalyst may then be heated in hydrogen.

1050. Backhaws ³² arranges metallic gauze disks (copper, chromium, nickel or iron) transversely in a tube, with or without separating rings. The surface of the gauze is corroded by passing an oxidizing gas (air) charged with acetic acid vapors. The resulting acetate film is heated *in situ* forming the oxide, which is then reduced in a current of hydrogen at $\pm 300^{\circ}\text{C}$.

This form of catalyst is particularly adapted for the production of aldehyde and hydrogen by the treatment of alcohol vapors at 300°C . This is, of course, a dehydrogenation.

1051. In somewhat similar fashion Hagermann and Baskerville ³³ employ nickel sheet, wire, or the like, with a surface layer of oxide in shapes specially adapted to the conditions of use ("tarnished shapes"). The metal preferably contains a small percentage of cobalt.

1052. Catalyst Prepared Electrolytically. Lush ³⁴ prepares a nickel catalyst directly on the metallic surface. The surface is subjected to anodic oxidation in an alkaline electrolyte which will not dissolve nickel (e.g., sodium carbonate solution). The oxide so produced on the metal is reduced in the usual way with hydrogen. Here, again, we have a method that offers simplicity in regeneration.³⁵

1053. Schueler ³⁶ also forms catalyst and catalyst support in one. Disks of woven wire, or of perforated sheet, or a spiral strip of metal with distance pieces corrugations, ribs or projections are used. Uniform oxidation is secured by anodic oxidation in an electrolytic bath.³⁷

1054. In another modification ³⁸ Schueler places the catalyst material in cages assembled on one or more perforated tubes through which the hydrogen is supplied.

1055. Pure Nickel Oxide by Anodic Oxidation. Iki,³⁹ chiefly with the object of obtaining a catalyst free from sulphate, which he says always persists when the carbonate or hydroxide is precipitated from the sulphate, prepares oxide by anodic corrosion of nickel. Pure sheet nickel is used and is electrolyzed in 0.1- or 0.05-normal sodium or potassium hydroxide or carbonate. Anodic solution takes place slowly at first in alkalies, and green nickelous hydroxide collects on

³¹ Brit. Pat. 162,370, 1920.

³² U. S. Pat. 1,400,204, 1921. Cf. Badische Co. Catalyst, para. 636, page 59.

³³ U. S. Pat. 1,238,137, 1917.

³⁴ U. S. Pat. 1,519,035, Dec. 9, 1924. See Chapter XXXVII.

³⁵ The process is described in an article by Lush, *J.S.C.I.*, 1923, 219T; its application to experimental investigation in a paper by the same author on "Kinetics of Hydrogenation," *ibid.*, 1924, 43, 11, 53T-56T.

³⁶ Brit. Pat. 274,952, Apr. 28, 1926, reff. to Brit. Pat. 273,045 (next para.).

³⁷ *Suppl. J.S.C.I.*, Oct. 14, 1927.

³⁸ Brit. Pat. 273,045, Dec. 31, 1926; *Suppl. J.S.C.I.*, Sept. 16, 1927.

³⁹ *Ind. Eng. Chem.*, 1928, 20, 472; *J. Soc. Chem. Ind.*, Japan, 1928, 31, 1; *Brü. Chem. Abst.*, 1928, 377A.

the anode, which is gradually oxidized to black adherent nickelic hydroxide. Adding 5–10 cc. of alcohol per liter prevents this oxidation and only nickelous hydroxide is formed, which easily comes off the anode. A voltage of 4–7 is used and a current density of 0.01 amp. per sq. cm. If the electrodes are separated by a suitable diaphragm, the alkali collects in the cathode space and at the anode are only nickel hydroxide and pure water. This favors the recovery of the alkali and the purification of the precipitate. The tendency of the nickel hydroxide to adhere to the anode is less in carbonate solution than in the hydroxide solution.

COLLOIDAL NICKEL CATALYSTS

1056. It was inevitable that experimenters should be tempted to devote labor to trying out colloidal nickel as a hydrogenation catalyst. Experience has, however, shown that not much satisfaction is afforded by the use of certain forms of highly colloidal catalysts of other than noble metals. In addition to offering negligible positive advantages, certain of these colloidal base metal catalysts are endowed with serious drawbacks. In some instances they are subject to sudden coagulation and to slow decomposition: they increase the difficulty of separating the finished product from the catalyst to an extent dependent on the character of the dispersion.

Thomas ⁴⁰ finds that while an active catalyst can be made in this manner, its activity, in spite of its enormous surface, is considerably lower than that of a nickel on kieselguhr prepared by reduction with hydrogen as described in para. 1034. An electric arc was formed under distilled water between two nickel electrodes, using a current of 8 amperes from 150 volts. It was found, under these conditions, that the disintegrated nickel was in such a fine state of division that no appreciable signs of coagulation were noticeable after the lapse of seven days. In order to transfer this catalyst into oil, the latter was added to the water containing it and the water evaporated off under diminished pressure. Its activity was determined by using it in 0.15 per cent concentration for hydrogenating cottonseed oil at 180° C., and comparing the rate of hydrogen absorption with that obtained by means of a supported catalyst using the same concentration of nickel. The iodine absorption of the cotton-seed oil was 111.0, corresponding to a total possible hydrogen absorption of 1040 cc. at 17° C. for 10 g. of the oil. The results were as follows:

Time (minutes)	Temperature, 180° C.	
	Hydrogen Absorption (cc.) *	
	(a)	(b)
5	142	41
10	256	73
15	321	102
20	380	130
25	435	149
30	478	165

* (a) refers to a catalyst prepared according to the method described in para. 1034 and (b) according to the present method.

⁴⁰ *Loc. cit.*

1058. It will be seen from the above figures that the activity of a catalyst prepared by electrical comminution under conditions which were found to give the most active preparation, is not more than one-fourth that of a supported catalyst prepared by reduction in hydrogen at 350° C., although the surface area of the former is much greater than that of the latter. If currents much higher than 8 amperes were employed the catalyst was not obtained in as finely divided a condition and its activity fell below that indicated above.

1059. Colloidal solutions of nickel can be prepared by the reduction of solutions or suspensions of nickel salts in glycerol containing gelatin or gum arabic as a protective colloid (C. Kelber, *Ber.* 1917, **50**, 1509). Thus, a solution of nickel formate and gelatin in glycerol at 200–210° when submitted to the action of a stream of hydrogen assumes a chestnut-brown color. The colloidal solution remains unaltered in air and is miscible with alcohol. On treatment with water and centrifuging, the colloidal metal is deposited as a brown solid containing 25 to 30 per cent of nickel. This again yields colloidal nickel solutions in dilute acetic acid, acidified water, glycerol, or alcohol. Hydrazine hydrate, formaldehyde, hydroxylamine, and hypophosphorous acid can be used as reducing agents and the nickel formate can be replaced by nickel acetate or freshly precipitated nickel hydroxide.⁴¹

1060. Nickel Sols in Toluene and Benzene. Hatschek and Thorne⁴² prepared sols containing 1.0484 g. of nickel per liter, by decomposing by heat nickel carbonyl in mixtures of benzene and toluene containing a small amount of rubber as a protective colloid. Sols, so prepared, can be concentrated considerably, without coagulation, by evaporating the dispersing medium.

1061. A disturbing feature of this work was the formation of a gelatinous, green precipitate when even small quantities of air had access to the solution. The precipitate formed rapidly when the stock solutions of nickel carbonyl used in the main investigation were exposed to the air. When these solutions were thereby rendered too weak to be of use for the preparation of the colloidal solutions, the precipitate was filtered off and air-dried (Found: Ni = 39.63, 40.11; CO₂ = 15.92, 16.21 per cent). It lost water (22.53 per cent) at 120° and became yellow, and was converted into black nickel oxide on ignition.⁴³

1062. Paal and Brunjes state that sodium protalbinat and lysalbinat exert only a relatively slight protective action on sols of nickel hydrate and that it is impossible to obtain sols of high nickel hydrate content by their use. The preparation of stable hydrosols containing 6 to 10 per cent nickel hydrate is described.⁴⁴

1063. Nickel Catalysts Prepared by Mechanical Subdivision of Massive Metal. In 1920 Elder made known a procedure for obtaining nickel catalyst whose essential novelty consisted in the mechanical reduction of metallic nickel to a degree of fineness permitting of its use as a hydrogenation catalyst.⁴⁵

1064. The means used are mechanical attrition, as in a ball mill, with or without an abrasive, in the presence or in the absence of an oil. The oil may be the substrate of the hydrogenation, in which case hydrogen may be introduced and the operations of preparing the catalyst and using it for hydrogenating the oil may be simultaneous.

⁴¹ *Chem. Soc. Ann. Rep.*, 1918, **25**, 29.

⁴² *Roy. Soc. Proc.*, 1923A, **103**, 276; *J.S.C.I.*, 1923, **42**, 627A.

⁴³ Thorne, *Trans. Chem. Soc.*, 1924, **125**.

⁴⁴ *Ber.*, 1914, **47**, 2200; *Chem. Abst.*, 1914, 3275.

⁴⁵ U. S. Pats. 1,331,903, 1,331,904, 1,331,905, 1,331,906, Feb. 24, 1920.

1065. In 1922 Richardson ⁴⁶ described a slight modification of Elder's process. This consisted in grinding in water instead of dry, or in oil.

1066. These innovations received much publicity, whose tone suggested that a great revolution was about to take place in the hydrogenation industry by the introduction of such new methods. It is, however, understood that the processes of Elder and of Richardson have not received extensive application.

1067. Thomas ⁴⁷ quotes Richardson (*Chem. and Met. Eng.*, 1920, **22**, 795: to the effect that action of mechanically prepared nickel catalyst in the hydrogenation of oils is somewhat different from that of chemically prepared catalysts. The latter exhibit their highest activity at the start, while the activity curve of the former shows a considerable rise at the commencement of hydrogenation, which may last for some time before the curve reaches its peak and begins to decline. Thomas goes on to remark that this peculiarity is reminiscent of so-called nickel oxide catalysts,⁴⁸ which have a higher activity when employed on a second or third occasion than when freshly used, a fact obviously due to progressive reduction. A surface layer of oxide may be formed under the conditions of preparation of the catalyst and would be reduced during the hydrogenation, as some forms of nickel oxide can be slowly reduced at temperatures in the neighborhood of 200° C. and, according to Sabatier and Espil (*Chem. Zeit.*, 1913, **37**, 1121), even at 150°–160° C.

1068. A flaky form of nickel catalyzer is brought forward by Hagemann and Baskerville ⁴⁹ to replace nickel supported on an inert carrier. They observe that the application of the latter type of catalysts involves a number of technical difficulties; for instance, on account of their finely divided state, such catalysts cannot be readily and satisfactorily separated and recovered from the fats, and, owing to their density, do not remain well suspended in the oil treated, when such suspension is desired. The use of a metal precipitated upon an inert carrier, such as kieselguhr, they note, has not given entirely satisfactory results, probably for the reason that only a small part (one side) of the film of the precipitated metal comes into actual contact with the liquid to be reduced and the hydrogen, and the remainder of the metal is consequently inactive, since the reacting materials cannot come into contact therewith. Other stated objections to the use of such a catalyst are the process of revivification is quite an expensive undertaking, since the metal must be dissolved in an acid, and reprecipitated upon kieselguhr; that it is difficult to obtain a catalyzer by precipitation and reduction methods, which is free from oxides and other impurities; and that fatty oils hydrogenated with such finely divided catalysts will contain metallic soaps, such as soaps having a nickel base, which are undesirable from economic and hygienic standpoints. Hagemann and Baskerville observe that metals having catalytic activity, such as nickel, or cobalt, brought into a state of extremely thin films, or flakes, by mechanical, chemical or galvanoplastic processes, as, for example, by the method shown by Edison,⁵⁰ offer technical advantages as catalysts in the hydrogenation of fatty oils. These films, or flakes, are obtainable in a state of high purity, and may be employed either in the metallic (pure) state or after being partially oxidized. Films can readily be prepared, having a thickness of from one twenty-thousandth to one forty-thousandth of an inch, and accordingly the efficiency of a given weight of a catalytic metal, for example, nickel, when applied in this form, is high, owing to the large amount of exposed surface. Such films, or flakes, will, on account of their extreme thinness, readily float and remain evenly distributed throughout the whole mass of

⁴⁶ U. S. Pat. 1,419,986, June 21, 1922.

⁴⁷ *Loc. cit.*, p. 7.

⁴⁸ See Chapter XII.

⁴⁹ U. S. Pat. 1,083,930, Jan. 13, 1914.

⁵⁰ U. S. Pat. 865,688, Sept. 10, 1907. See also 821,626, May 29, 1906.

fats or oils.⁶¹ The separation of the hardened products from the flaky nickel, cobalt, etc., is said to be accomplished without difficulty. In the revivification and recovery of the catalyzer for subsequent use it has been found that flaky metals, as nickel, etc., admit of economical treatment, for the flakes retain their physical form. In this revivification the flakes, or films, from which the fat has been removed (for example, by extraction with a suitable solvent) are subjected to superficial oxidation followed by reduction with hydrogen at, say, 300° C., or higher, in a current of oxygen or air, or by treatment with oxidizing agents in liquids in which the metallic flakes are suspended. In such a manner Hagemann and Baskerville state they can repeatedly produce freshly reduced surfaces to both sides of the metal flakes, or films, without having recourse to conversion of the metal into a soluble salt, precipitating, igniting and reducing.

1069. Eldred⁶² does not regard a finely divided catalyst as desirable as one having a catalytic metal welded to a heat-conducting support. He states that since the amount of such catalytic action performed in a given time unit in a body of gas is strictly proportionate to the exposed surface of catalyzing metal, it is customary to use such metals in finely divided form, sometimes as masses of powder and sometimes as powders adhering to and held by inert porous materials, such as asbestos, glass wool and the like, but that these expedients while giving great surface to a given amount of metal do not give a proportionately great exposure of such metal to the gases or vapors to be treated. It is substantially impossible to drive or distribute gases uniformly throughout a body of powder, and in passing gases over a body of such powder it is generally only the top layers of the powder which display a maximum activity, underlying layers not functioning to any great extent. Use of very thin layers of powder of course necessitates unduly extended shelf surface. Eldred observes that nearly all catalyses are exothermic reactions, heat being developed by the action, and frequently the amount of heat is rather large. And as it is usually desirable to work within comparatively narrow temperature limits, keeping and maintaining the catalytic metal within a few degrees of some definite temperature, this evolution of heat may become a serious matter. Nearly all the catalytically acting metals in the form of powders are relatively poor conductors of heat. When, for example, platinum is distributed through a mass of such a heat insulator as asbestos, it is very hard to prevent the accumulation of reaction heat in the metal. Hence Eldred proposes a catalytic body comprising the catalytic metal in the form of a very thin continuous layer of film supported by masses of better heat-conducting metals weld-united to such layer of film and therefore in absolute metallic union therewith so that by controlling the temperature of the carrying metal the temperature of the film or layer can also be controlled. A catalyst may be made by welding a sheath or coating of platinum on a billet of copper or steel and "coextending" the joined metals to form wire or sheet metal. If 3 to 10 per cent of platinum be placed on the original billet and coextension be performed with care, the wire, sheet or leaf metal formed will also have 3 to 10 per cent of platinum, but this thickness in such coextended ware will correspond to an extremely tenuous layer. Cobalt and nickel may be united to steel or copper billets, and the duplex or compound billets extended in similar manner to produce catalysts having film coatings of cobalt or nickel. The cobalt or nickel may be united to the underlying core metal directly or through a linking layer of another metal such as gold, silver or copper. Eldred mentions the cobalt and nickel catalysts as useful in hydrogenation reactions.

1070. Catalysts from Alloys. Nickel catalysts are prepared from alloys of nickel with silicon or aluminum by dissolving away the silicon or the aluminum.⁶³

1071. An alloy of copper, nickel, and iron with magnesium, zinc, and sometimes calcium is oxidized by heating in the air or by pouring it in thin streams through heated air, and the resulting mass of oxides is crushed and used as a catalyst, with or without partial reduction in hydrogen.⁶⁴

⁶¹ The author has made use of a form of flaky nickel derived from nickel carbonyl in hydrogenating oils and has found this form of the metal to be satisfactory from the catalytic standpoint.

⁶² U. S. Pat. 1,043,580, Nov. 5, 1912.

⁶³ U. S. Pat. 1,628,190, May 10, 1927, to Raney. Cf. 1,563,587, Dec. 1, 1925, to same patentee. Cf. para. 681.

⁶⁴ *Brit. Chem. Abst.*, 1929, 480B; *Brit. Pat.* 309,743, Apr. 20, 1928, to Howards & Sons, Ltd., Blagden and Clark.

1072. Porous Metal Catalysts. Alloys may be treated with a solvent having a selective action. To obtain porous copper brass is treated with sodium hydroxide: the resulting sodium zincate is dissolved out with hydrochloric acid: the

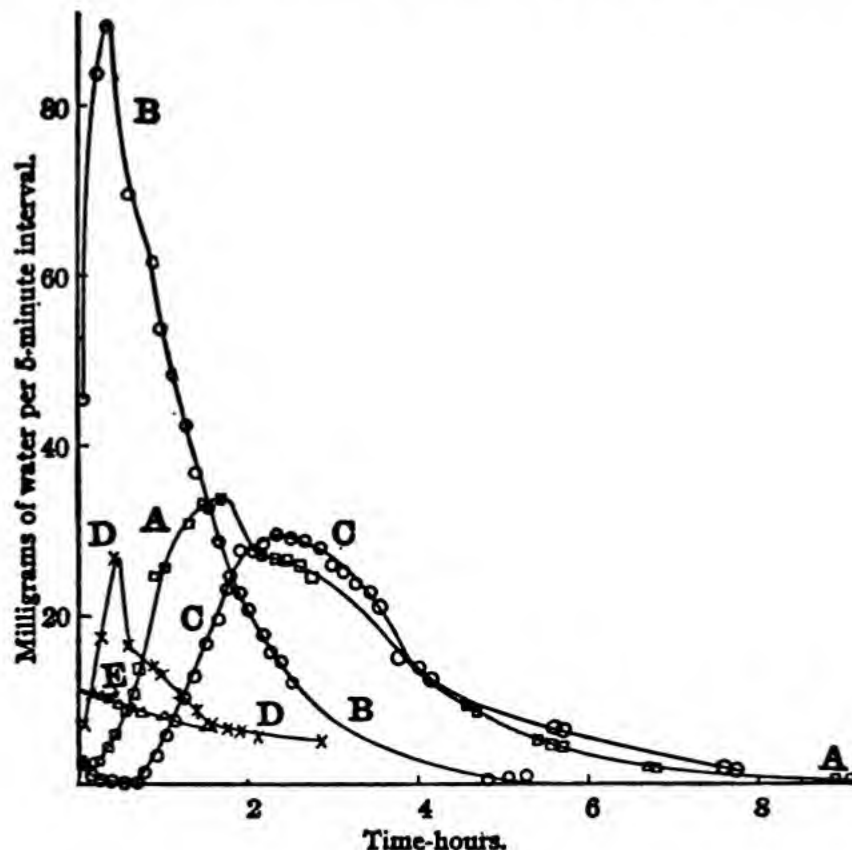


FIG. 14a.

Curves of reduction of nickelous oxide by hydrogen, as determined by Benton and Emmett.¹⁵ Curve A shows reduction at 188° C. of the oxide prepared by ignition of nickel nitrate at about 400° C. Curve B, similarly prepared oxide, reduction at 208°. Curve C, oxide from nitrate in current of nitrogen at 360°, reduction at 188°. D, reduction at 250° C. of oxide prepared at 525°. E, reduction at 280° of commercial oxide.

copper remains in a porous form. Other metals, such as nickel (from zinc and aluminum alloys) iron (from ferro-silicon) and tin (from tin-sodium) as well as mixtures and the solvent can be used. Porous metals of this kind are catalytic.¹⁶

¹⁵ See paragraphs 1022-1023, page 116, this volume: *J. Am. Chem. Soc.*, 1924, 46, 2728.

¹⁶ Brit. Pat. application 282,112, convention date Dec. 13, 1926, by I. G. Farbenind. A.-G.; *Chem. Age* (London), 1928, 18, 150.

CHAPTER XI

PREPARATION OF NICKEL CATALYSTS ¹

1100. The methods proposed for the preparation of nickel catalysts may be classed as follows:

1. From massive metal:
 - (a) By fine division by mechanical means.
 - (b) Colloidal metal by electrical disintegration.
 - (c) Turnings, wire and the like, oxidized on the surface and reduced.
2. By reduction of oxide, hydroxide or carbonate in a current of reducing gas (usually hydrogen).
3. By heat reduction of nickel salt.
4. By ignition of nickel compound with carbonaceous material.
5. By heat decomposition of nickel carbonyl.
6. Use of unreduced (?) nickel salts of inorganic oxygen acids (e.g., borate, metaborate, silicate).
7. Use of nickel boride.
8. Use of nickel carbide.
9. Use of nickel hydride.
10. Specialized use of organometallic nickel compounds.
11. Replacement of nickel from solution of its salts by other metals.

1101. Unless incompatible with the nature of the catalytic material, inert supports, such as pumice or kieselguhr, may be employed, as may promoters usually in the form of other metals.

1102. At the time of the publication of the earlier editions of this work experience had not yet taught which of the numerous methods for producing nickel catalysts were really viable. It was therefore necessary to describe each alleged improvement in more or less detail. Since that period, however, the art has become more static or, at any rate, more stable. It now suffices to illustrate the principal methods in each class, laying stress on those which have proved of practical value or which seem suggestive.

1103. When tabulating the methods of preparing nickel catalysts (para. 1100) an order was adopted which seemed the logical one. In actual practice, both in the laboratory and in the factory, the second class (reduction of nickel oxide, hydroxide or carbonate in a current of hydrogen) is of great importance. For this reason, and especially because many experimental methods are found here, we will first deal with this class.

¹ Other metal catalysts are dealt with here, when methods of preparation are common to them and to nickel catalysts.

PREPARATION OF NICKEL CATALYSTS

LABORATORY METHODS

1104. For Hydrogenation in Vapor Phase. (1) Asbestos or pumice, thoroughly cleaned by treating with dilute nitric acid and washing, is ignited. The material so prepared is soaked in nickel nitrate melted in its own water of crystallization. The drained product is calcined at about 300°. It is then placed in the tube in which it is to be used and reduced in a current of pure, dry hydrogen at 350°. The catalyst should be allowed to cool in an atmosphere of hydrogen if it is not to be used immediately.

1105. (2) The following briquette preparation is recommended by Maxted² for such purposes as the hydrogenation of benzene. Nickel nitrate is dissolved in distilled water and to the solution magnesium nitrate is added in sufficient quantity to give with soda a weight of magnesium oxide equal to the nickel in the nickel nitrate. The mixed nitrates are precipitated with sodium hydroxide or carbonate, and the precipitate, after being washed with distilled water, is spread with a nickel or porcelain spatula, as a layer of about $\frac{1}{4}$ in. thick, on a clean, square sheet of nickel. The moist mass is conveniently divided into squares of suitable size by means of a needle mounted in a wooden holder, when it may be dried by the cautious and gentle application of a Bunsen flame to the supporting nickel plate. The briquettes are now placed in the reduction tube and reduced by a current of hydrogen at 350–400° C.

1106. For Hydrogenation in the Liquid Phase. A nickel catalyst for use in hydrogenating a liquid may be: (1) prepared separately and then mixed with the substrate;³ or (2) produced in the body of the liquid substrate. In most cases the temperature of reduction is higher than the minimum temperature of catalytic action. Therefore, the first method is preferred for the preparation of catalysts to be used with volatile liquids.

1107. (1) Separate Preparation. (a) Without support. The oxide, hydroxide or carbonate is prepared as before, the first by calcination of nitrate, the others by precipitation, washing and drying. A convenient way to effect the reduction is to place the dry material in a distilling flask, which must not be more than a quarter full. The flask and its contents may be placed on a sandbath and heated in a current of pure dry hydrogen at 320°–350° C., with frequent shaking to renew the surface for reduction. With a fairly rapid current of hydrogen and a 300-cc. flask one-quarter full of nickel oxide, two to three hours' treatment will produce sufficient reduction.

(b) With inert support. If it is desired to extend the nickel on a support, the precipitation must be done in the presence of from 2 to 10 parts of kieselguhr (or other inert carrier) to 1 of metallic nickel, and with constant stirring; the temperature of reduction should be about 420° C.

1108. (2) Reduction in the Liquid Substrate. This method is suitable for the hydrogenation of non-volatile liquids, such as the fatty oils. In such conditions the reduction of the oxide takes place at comparatively low temperatures. An active catalyst is obtained by reducing nickel oxide in cotton oil at 260° C.

² Catalytic Hydrogenation, p. 8.

³ The substrate is the substance undergoing hydrogenation.

1109. Nickel catalysts reduced dry should be allowed to cool in an atmosphere of hydrogen or of carbon dioxide and should be used as soon as possible.

1110. The methods used or proposed for the commercial preparation of hydrogenation catalysts from the oxide, hydroxide and carbonate of nickel do not differ in principle from the laboratory processes. Any classification must necessarily involve overlapping; the following is offered, therefore, as a rough division of the various methods according to their salient features.

1. Straight reduction in hydrogen.
2. Reduction in two stages: First at 200°–300° and 760 mm.; second, at the same temperature and at 4–5 atmospheres pressure.
3. Surface reduction.
4. Reduction in various liquid (or melted) media, such as paraffin wax, vaseline, fat, naphthalene, toluene.

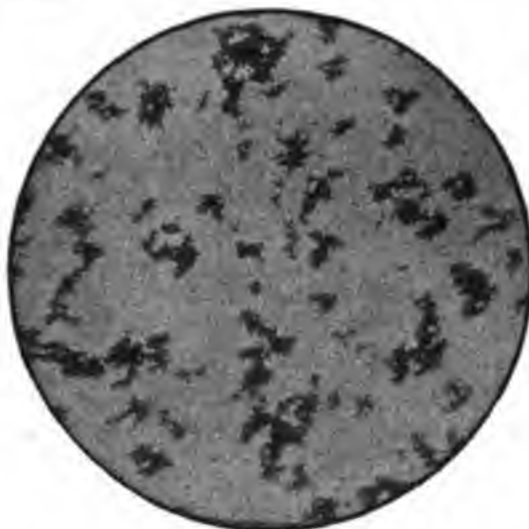


FIG. 15.

Photo-micrograph of nickel precipitated in cottonseed oil by the action of hydrogen on nickel resinate dissolved in the oil. $\times 100$.

1111. In the cases where the catalyst is reduced dry some precaution must be taken against oxidation. Usually this consists of cooling in hydrogen or in carbon dioxide, but it is even better to incorporate the catalyst immediately in a protective medium such as wax, fat or hardened oil.

1112. Mashkilleisson ⁴ lays down that sodium carbonate and not the hydroxide must be used for precipitating aqueous solutions of nickel salts in the preparation of catalysts for oil hardening. Owing to the obstinate occlusion of sodium hydroxide, silicate is formed on reduction and the activity is impaired. Clearly this objection applies only to reduction in the dry way in non-metallic roasters. As a matter of practice soda-ash is the preferred precipitant—if only because of its cheapness.

1113. Cooling Nickel Catalyst in Carbon Dioxide.⁵ Two samples of a nickel catalyst prepared in the usual way and cooled in an atmosphere of carbon dioxide were used for the

⁴ Oil and Fat Ind. (Russia), **1926**, Nos. 4–5, 53; *Chem. Zentr.*, **1927**, I, 2868.

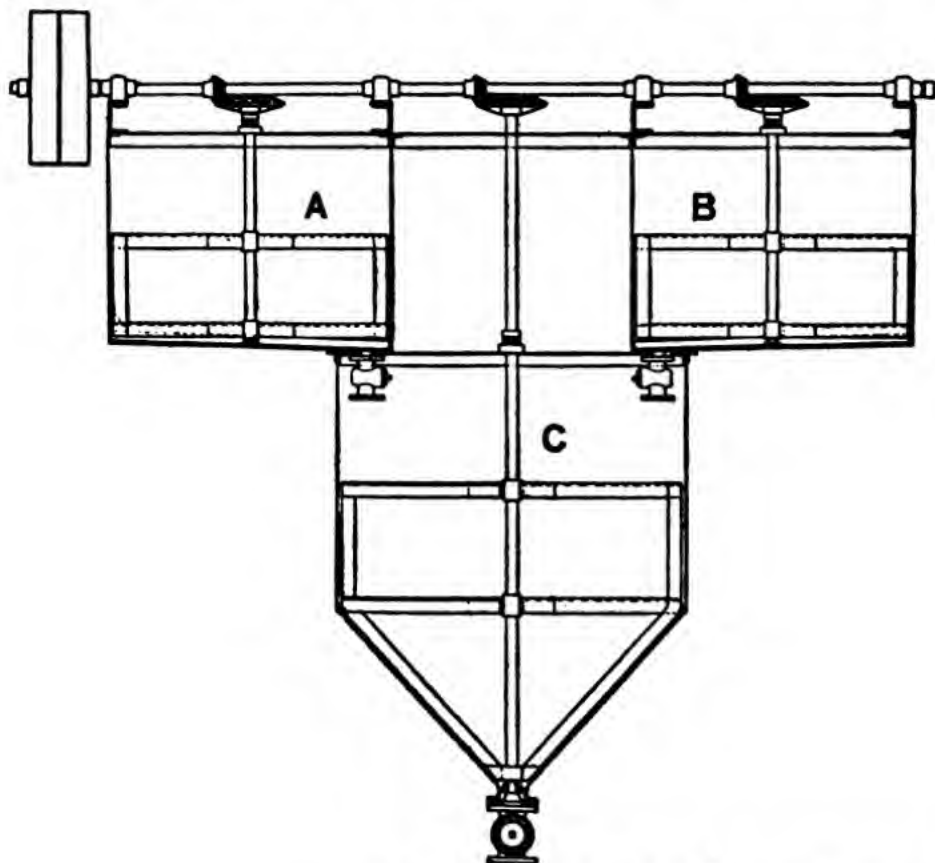
⁵ Bag. *Masloboino-Zhirovoye Delo.*, No. 3, 6 (1928).

following observation. The first sample was left exposed to the air for one month, and 0.34 per cent mixed with 99.66 per cent of cottonseed oil. The second sample was mixed with the same oil in the same proportion immediately after the nickel catalyst was prepared. The table shows the action of both catalysts.

Time of Hydrogenation	Temperature of Hydrogenation	Iodine Number	
		Sample No. 1	Sample No. 2
1 hour	240°	79.3	75.6
2 hours	240°	59.4	47.6
2½ hours	240°	47.4	36.8

Because of the treatment of the nickel catalyst with carbon dioxide its deterioration can be considered negligible.

1114. The number of different kinds of apparatus for the preparation of simple nickel catalysts is very large. It would serve no useful purpose to attempt an exhaustive description. Typical examples, only, will, therefore, be dealt with.



(Courtesy of John Thompson [Gas Developments] Ltd.)

FIG. 16.

1115. Preparation of Nickel Hydroxide or Carbonate. This may be effected in the apparatus shown in Fig. 16. It consists of two solution tanks, A and B, provided with

mechanical or compressed air agitation. In these, suitable weights of nickel sulphate and sodium hydroxide or carbonate, respectively, are dissolved and the solutions produced are caused to flow into the third tank *C*, which has a conical or inclined bottom, according to the method of agitation employed. In this tank, a sludge of nickel carbonate or hydroxide is produced and is pumped by means of a filter pump through filter presses.

1116. The filter cake of nickel carbonate or hydroxide thus obtained is well washed in the press by means of running water and is subsequently removed and dried.

1117. Two types of drier are employed, of the stationary and of the rotary type respectively. In the stationary type of drier, the filter cake is subjected to the action of a current of warm air in a drying room of special construction.

1118. The rotary type of drier is of special service where quick drying is required. In this, the filter cake is continuously broken up by means of massive agitators and is subjected during this process to the action of a current of warm air. During the drying operation the apparatus is raised to a suitable temperature by means of a steam jacket.

1119. **Reduction of the Dried Catalyst.** The nickel carbonate or hydroxide, after being thoroughly dried, is subjected to a preliminary grinding operation, by means of which it is reduced to an impalpable powder. The ground catalyst is then conveyed to the reducing plant.

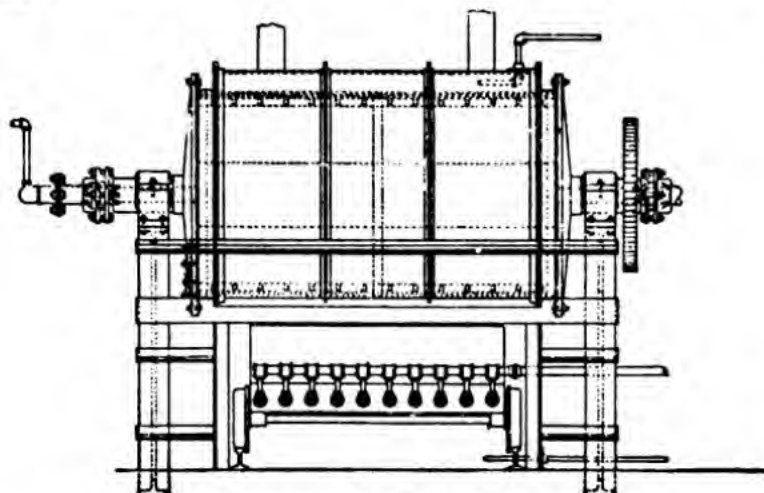


FIG. 17.

1120. The type of reducer employed consists of a welded steel container, which is heated to a temperature varying from 300° to 350° C. by means of a surrounding brickwork chamber. During the reduction of the catalyst to metal, a current of hydrogen is passed through the reducer, and the reduction chamber, which is fitted with an internal agitating arrangement, is rotated slowly by means of the gearing shown.

1121. After reduction, the reduced nickel is allowed to cool in hydrogen, and is mixed with a small quantity of oil with special precautions. This cream of oil and catalyst is pumped in the required quantities into the hardening vessel, and is there incorporated with the main quantity of oil used for hydrogenation.

1122. An apparatus employed by Kayser⁶ for reducing metallic oxides with hydrogen, is shown in side elevation in Fig. 17 and in vertical cross-section in Fig. 18. It consists of a rotary drum supported by hollow trunnions, and provided with vanes for agitating the material. The latter is introduced through a manhole. A reducing gas is introduced through one trunnion and escapes through the other. Entrained matter is removed from the used gas by a trap and water seal. The drum is heated from beneath by gas burners mounted on a removable carriage. A jacket surrounds the drum, forming a space through which the products of combustion pass to the stacks at the top. When the charge has been reduced, the burner carriage is removed and steam is blown around the drum until the latter has cooled somewhat. Finally, water is sprayed on the drum for a brief period and the cooled contents are then removed.

⁶ U. S. Pat. 1,134,745, April 6, 1915.

1123. Lane has devised an apparatus and process for the industrial preparation of catalyst.⁷ A metallic circular air-tight pan is provided with a vertical shaft, carrying two arms, which are curved helically in a horizontal plane. The arms carry sliding teeth, which rest on the bottom of the pan, and the shaft may be rotated in either direction, so that the material in the pan may be forced outwards or inwards as desired. The material is fed from a hopper, provided with an oscillating valve, and finally discharged through a column. The pan is heated by an annular burner ring. Oil or other coating substance for the catalyst is first fed into the apparatus to seal the lower outlet of the column, and a reducing gas is injected through a pipe. The raw material is then fed from the hopper, and heating is continued till water ceases to be condensed in the condenser. The rotation of the shaft is then reversed, and the material thereby collected towards the center of the pan and discharged into the coating liquid. The apparatus is applicable for the manufacture of finely divided reduced nickel for the production of stearin by hydrogenation of oils.⁸

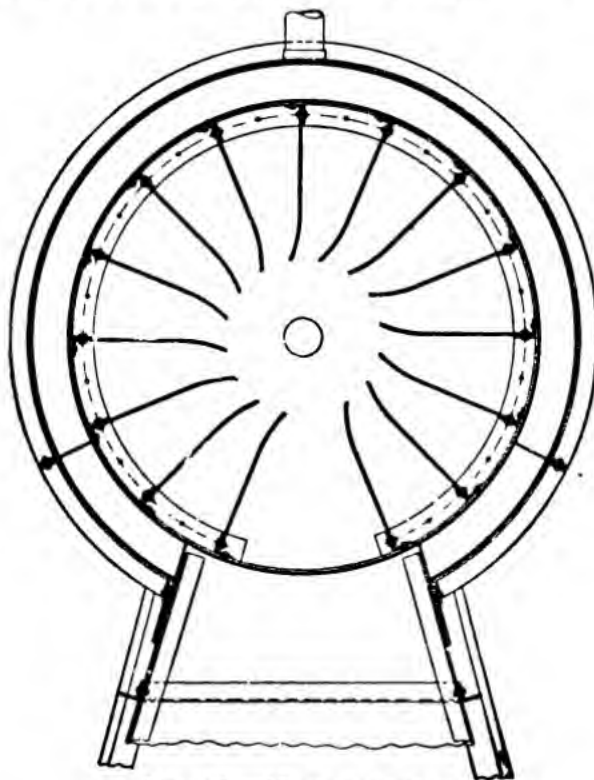


FIG. 18.—(CROSS-SECTION.)

1124. On the large scale the manufacture of catalyzers by reduction of the oxide of a metal in a current of hydrogen has been found to bring with it a train of difficulties. A method of reducing catalyzer in a continuous manner⁹ which simplifies the operation to a considerable extent is shown in Fig. 19. A charge of the material to be reduced is fed from the hopper and feed arrangement into a series of horizontal parallel conveyors 1, 2, 3 and 4, into which a current of hydrogen gas is introduced by the pipe 5. These conveyors connect one with another alternately so that the material travels in one direction through a given conveyor, then falls into the conveyor beneath and travels in an opposite direction. At the same time the material is heated to the proper temperature of reduction and throughout its travel is in contact with a counter-current of hydrogen. Thus, the more nearly reduced material is constantly progressing into a zone of purer hydrogen, while the fresh raw material

⁷ Brit. Pat. 115,924, June 11, 1917.

⁸ *J.S.C.I.*, 1918, 297A.

⁹ Ellis, U. S. Pat. 1,078,541, Nov. 11, 1913.

meets hydrogen charged with steam. In this manner conditions of reduction are so facilitated that the use of a great excess of hydrogen to remove the steam does not become necessary. After the catalyzer has been reduced it may be mixed with oil in another conveyor and be subsequently carried to a grinder or beating apparatus where the coarser particles are broken down. Another form of catalyzer reducing chamber is shown in Fig. 20 and consists of a

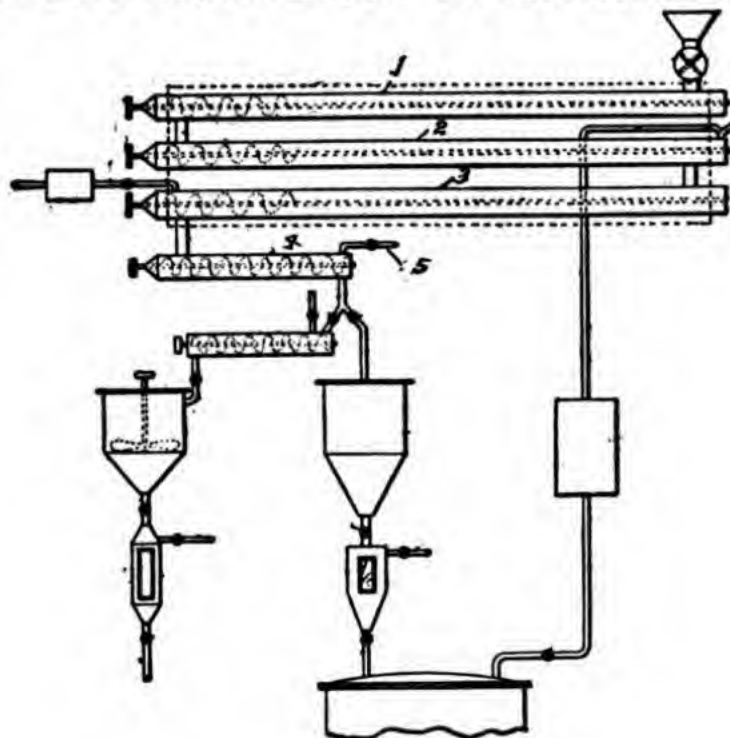


FIG. 19.

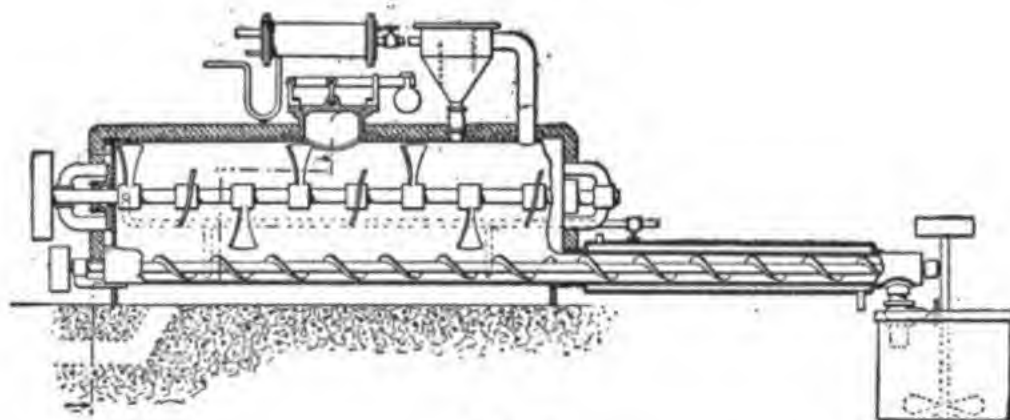


FIG. 20.

closed chamber equipped with a stirrer and with a conveyor to remove the reduced material.¹⁰

1125. Morey and Craine¹¹ describe a form of apparatus for making catalytic material which comprises in its main features an inclined tube or conduit through which the catalytic raw material flows downwardly, either by gravity alone or by gravity assisted by a jarring or

¹⁰ Ellis, U. S. Pat. 1,084,202, Jan. 13, 1914.

¹¹ U. S. Pat. 1,167,915, Jan. 11, 1916.

shaking action, and through which the gas flows upwardly, the tube or conduit being heated in any suitable manner, for instance, by direct flame, superheated steam or electrical current.

1126. In Fig. 21 is shown a side elevation of this apparatus. 10 represents the inclined tube in which the material is subjected to the action of a reducing gas, and to the upper end of which the raw material is supplied from a feed receptacle 11 by a flexible pipe 12. This inclined tube is supplied with gas from a gas holder 13 by means of a flexible pipe 14 which is connected with the lower portion of the tube. The treated material is discharged from the lower end of the latter into a closed receptacle 15 by a flexible pipe 16 without exposure to the atmosphere. The gas escapes from the upper end of the tube and is conducted by a flexible pipe 17 to a scrubbing apparatus 18 in which objectionable matters are separated from the gas and from which the purified gas is returned to the gas holder 13, to which fresh gas is supplied as may be necessary. Circulation of the gas through the apparatus is maintained by a pump 27. The inclined tube or conduit is heated to a reducing temperature. When diatomaceous earth impregnated with nickel hydroxide is treated, a temperature of about 550° F. is preferred. The treating tube may be inclined at such an angle, usually about 42°, that the material will flow through the tube by gravity, or as shown in the illustration, the

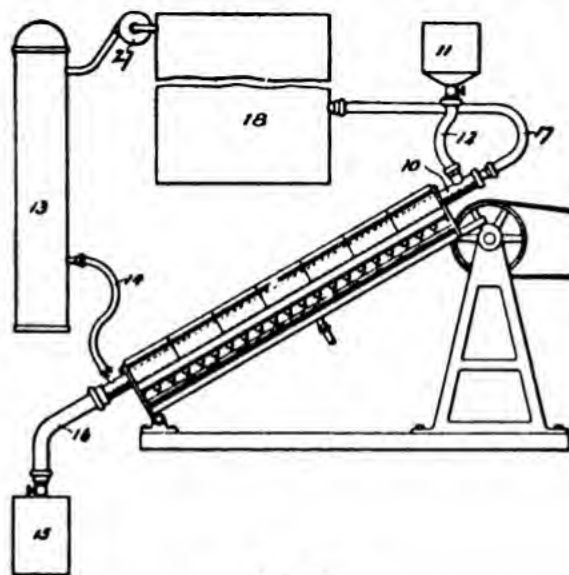


FIG. 21.

tube may be inclined at a less angle and a jarring or shaking mechanism be provided for causing the material to flow properly. As shown, the carrying frame for the tube is movably supported by a hinge at its lower end and rests at its upper end upon a rotating cam.

1127. An apparatus employed by Wilbuschewitsch,¹² Fig. 22, for the reduction of nickel compounds consists of a cylindrical drum *b* mounted to rotate on rollers *m* and provided with a heating jacket *o*. The material is charged into the drum through an inlet opening *n*. To one of the end plates of the drum a tubular shaft *c* is secured which, with its free end, is guided in a stuffing box *k* supported in a lateral stud of a tubular receptacle *d*. On the shaft a spur gear *q* is mounted which is in mesh with a pinion *q*₁ adapted to be rotated by means of a belt pulley *r*. By means of the gearing *q*, *q*₁ the drum *b* is slowly rotated, and during such rotation it is heated to about 500° C. Hydrogen is then forced into the drum through a pipe *a* located coaxially within the hollow shaft *c* and connected at one end to a tube *i*. The hydrogen is passed through the material to be reduced, and from the latter it is successively conducted through an automatically operating dust collector 9 connected to the retort, a cooling worm *f* and purifying vessels *g*, *g'* containing respectively acid and caustic soda lye, or a similar purifying medium. After thus being regenerated it is returned by means of a pump *h*. The water produced by the reduction is condensed in the coil *f* and is dropped from the coil *f* into the vessel *d* from which it is withdrawn through an overflow *e*. The dust collector 9 by means

¹² U. S. Pat. 1,029,901, June 18, 1912.

of which the hydrogen escaping from the drum is prevented from carrying along particles of dust is constructed in the form of a worm conveyor *l*. The dust moves through the hollow shaft *c* in the direction of the gas flow and owing to the difference in the speed of the gas and dust the latter is deposited on the bottom of the shaft *c*, and is conveyed back into the retort by the worm *l*.

1128. Filtration Apparatus for Washing Nickel Catalyst.¹³ An open container is provided with a discharge pipe and valve leading to a second container. Close to the bottom of the first container are two perforated plates carrying a filtering cloth, the catalyst and solution above the plates being mechanically agitated. The drum-container, provided with an level-gauge, is connected to a vacuum pump and discharges into a third container.¹⁴ It is not clear whether this is meant, as stated, for washing the catalyst or, as seems more probable, for washing the carbonate or hydroxide before reduction.

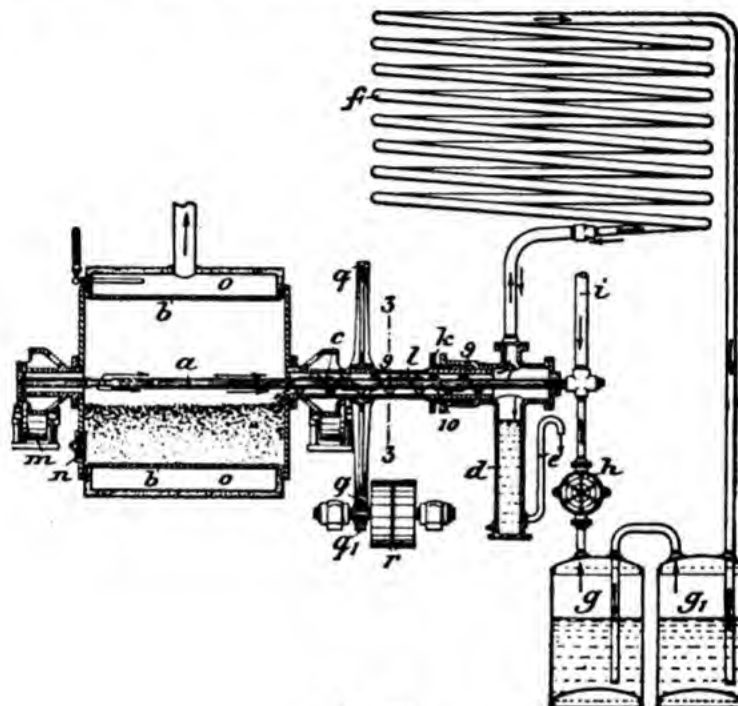


FIG. 22.

1129. Reynolds¹⁵ notes that the danger of explosion when using hydrogen to reduce catalytic raw material is a serious menace because the reduction of the material being treated is usually effected in a drum or cylinder that is heated by a flame and the slightest defect in the drum would permit the escape of hydrogen into the flame with disastrous results.

1130. Instead of hydrogen, Reynolds finds ammonia may be used, or even carbon monoxide if rendered non-inflammable by admixture with an inert gas. Also it is possible to mix hydrogen with inert gas so that it is rendered non-explosive. This inert gas may be either carbon dioxide or nitrogen or a mixture of both, their proportions being immaterial so long as the percentage of reducing gas does not reach the explosive point. Reynolds states that even 5 per cent is non-explosive. He thinks that the inert gas tends to envelop the reducing gas in the mixture so that it is rendered non-explosive but does not combine

¹³ Russ. Pat. 2364, 1925, to Sosenski.

¹⁴ Brit. Chem. Abst., 1928, 877B.

¹⁵ U. S. Pat. 1,210,367, Dec. 26, 1916.

with it to change its reducing quality in any degree. While ammonia may be used alone, it may be also mixed with the inert gas. The preferred mixture is nitrogen, carbon dioxide and carbon monoxide and a method of making it is to draw air through burning coke in a closed container; washing the resulting product and then conducting it into the reducing drum. The air after passing over the coke becomes a mixture of gases containing approximately 78 per cent nitrogen, 20 per cent carbon dioxide, and 2 per cent carbon monoxide. This mixture is stated to be efficient as a reducing agent, is cheap to make and is non-explosive. The resulting catalyzer may be exposed to the atmosphere for about thirty minutes without detriment to its catalytic properties.

1131. Reynolds' process, however, never received much consideration industrially, despite an occasional explosion when reduction in the dry way was employed. For a number of years after the commercial beginnings of oil hardening, dry reduction by passing hydrogen through heated cylinders or drums containing the catalyst, in the making, was practiced almost exclusively. Much effort was expended in the design of apparatus which would eliminate some defect observed in earlier equipment. The pyrophoric nature of reduced nickel caused many failures. In one plant which the author visited during infant years of the oil-hardening industry workmen in the catalyzer department were just recovering from their surprise arising from the rather disastrous or at least astonishing results of opening a heated reduction cylinder, thereby allowing air to rush in over a great mass of pyrophoric nickel. In another plant the author found fairly large-scale equipment had been set up for hydrogenation. No provision had been made, however, for the safe transfer of catalyst from the reduction chamber to the oil. The equipment had been designed and erected on the basis of laboratory experiments which had been conducted at the plant. When ready for operation the catalyzer could not be produced in an active condition and as a result the plant had been abandoned. At the time of the author's visit the chemist in charge was still puzzling over the mystery of this uncatalytic catalyst. When conducting experiments in the laboratory he had reduced the catalyst in a small tube, which was then up-ended over a quantity of oil and the transfer of the catalyzer was thus made so rapidly that a part at least of its activity had been preserved. The slower operations of transfer on plant scale failed to duplicate the laboratory experiments in this respect, with the consequence that the catalyst was rendered inactive. These illustrations are given as an indication of the groping along dark ways which confronted the practical investigators of the early days.

The instability of the dry-reduced catalyst due to its pyrophoric tendencies led to the "sweeping out," treatment after reduction had been completed, by flushing the reduction apparatus with an inert gas, usually carbon dioxide or nitrogen, to remove the hydrogen which had been occluded by the nickel. The removal of the occluded hydrogen eliminated pyrophoric oxidation, but this step and various others necessitated by the exigencies of plant operation gave rise to the employment of complicated reduction apparatus, seemingly wholly out of line with the rather simple steps involved in dry reduction on the laboratory scale.

1132. A tremendous advance in simplicity of catalyst production and freedom from the hazards of explosion due to pyrophoric oxidation was made when the method of wet reduction was developed and introduced. By wet reduction as

distinguished from dry reduction we refer to the step of forming the catalyst in oil or other protecting medium. With the industrial introduction of the wet process another nuisance, namely, the physiological action of nickel dust disappeared. In carrying out reduction by the dry process on a large plant scale it was found hard to suppress the escape of nickel dust into the air of the catalyzer reduction room. The inhalation of nickel dust was found to have a bad effect on workmen. Wet reduction with its freedom from dust therefore was welcome.

1133. For a considerable period after the convenience of wet reduction became appreciated, nickel formate was extensively used as the raw material for preparing the catalyst. Although other organic salts of nickel were available, still the formate was not only easily prepared but also left no organic residues on reduction, advantages which were sufficient to make nickel formate the vogue for a period of years. After the tribulations and uncertainties of dry reduction, the formate catalyst was hailed as a blessing. To prepare the catalyst well-ground nickel formate simply was heated in oil at 240° - 250° C. and hydrogen passed through, yielding a finished catalyst in a period of time expressed in minutes compared with the hours of processing required in dry reduction.

1134. Although a part of the nickel formed by the decomposition of nickel formate possesses colloidal properties, the problem of filtration was not a serious one, as it was found that by the addition of a bulking or filtration agent, such as fuller's earth or kieselguhr, the nickel would be retained satisfactorily in the filter press. To avoid imparting a clay taste to the oil silex sometimes was used as a bulking agent.

1135. If one is to criticize the nickel formate process in any respect the temperature of the reduction 240° - 250° C. in oil perhaps should be mentioned. Suppose, for example, a plant is hardening cottonseed oil, and in order not to introduce any foreign oil into the charge to be hydrogenated likewise employs cottonseed oil as the medium in which the nickel formate is to be reduced. The reduction temperature is so high that the oil is slightly "scorched" and this impairment of flavor and color makes filtration of the nickel necessary if the plant is hydrogenating oils for edible purposes. That is, the batch of nickel concentrate in oil cannot be put directly into the hydrogenating tank charged with oil to be hardened, but must first be freed of the scorched oil by filtration and washing with fresh oil. To that extent the nickel formate process was troublesome. Of course when a plant was producing hydrogenated oils for various other purposes than to supply the edible field the entire concentrate containing the scorched oil could be introduced into the batch ready for hydrogenation.

1136. A lower temperature of reduction by the wet method therefore was contemplated which would eliminate the objection of introduction of a small proportion of scorched oil into a large batch of oil ready for hardening. There was needed a nickel compound which would become actively catalytic at the temperature of oil hardening, or approximately 180° C. Demand also would be made that such a catalyst should possess longevity in order that it might be used repeatedly. Such a catalyst was found, not in a simple nickel compound but in a nickel copper product. Copper alone has very weak hydrogenating powers on

vegetable oils, so weak indeed that its employment as the sole catalyst would be out of question for industrial purposes. Basic compounds of copper, such as the hydrate and carbonate as well as various organic salts such as the formate, however, possess the very valuable property from the present standpoint of undergoing reduction at a temperature lower than the corresponding nickel bodies. Furthermore, reduced copper catalyzes the reduction of nickel compounds and enables them to be formed at a temperature lower than normal.

1137. The observation was made that the presence of copper would permit nickel to undergo reduction at about 180°C ., that is, at the customary temperature of industrial hydrogenation of most vegetable oils. The use of a catalyst to make a catalyst accomplished a decided step forward in the field of commercial hydrogenation. Precipitated nickel carbonate previously had been used in wet reduction, although the temperature required was high. Since this temperature was higher than that required for nickel formate there was a greater degree of oil scorching, nevertheless nickel carbonate had its advocates. Cheapness perhaps was the especial recommendation for nickel carbonate. With the arrival of a recognition of the effect of copper as an aid to the reduction of nickel compounds use was made of a mixture of nickel and copper carbonates which satisfied the requirements of cheapness and ease of reduction at normal oil-hardening temperatures.

Such a mixture of carbonates may be easily prepared by precipitation of a solution containing nickel and copper sulphate by a solution of soda ash then washing and drying somewhat; although complete drying is not necessary and possibly not even desirable. The elimination of the last portion of the water during actual reduction in the oil is thought to be advantageous in engendering a greater spread of active catalytic surface. Copper is generally used in a minor proportion. One part of copper to four parts of nickel is fully adequate to initiate the reduction of basic nickel compounds at 180°C .

1138. To save the time which would be consumed in preparing the precise amount of catalyzer required for each charge of oil, it is customary to make a concentrate of reduced nickel and copper in oil of the same grade which is being hardened and to add this catalyzer-concentrate to the charge in the proportion which supplies the requisite content of nickel. This is usually one to two parts of nickel per thousand parts by weight of oil, the proportion increasing as the catalyst weakens through repeated use. Loss of catalyzer during filtration and handling is compensated by the addition of fresh quantities of the catalyzer-concentrate. When oils have been well refined and therefore are quite free from catalyzer poisons a catalyst may be used repeatedly merely by fortification from time to time with small additions of the fresh concentrate.

1139. The subject matter of the paragraphs immediately preceding (paras. 1131-1138) will be further discussed elsewhere in this volume. The development of nickel catalysts industrially gives rise to comment by the author on the seeming hindrance to advancement chargeable to vapor phase hydrogenation. Sabatier fostered hydrogenation in the vapor phase, naturally using for the purpose a catalyzer which had been made by dry-reduction. Normann, following the

teachings of Sabatier, put similar dry-reduced catalyst in a liquid (unsaturated oil) and found that the activity of nickel manifest in the vapor phase also was exhibited when such nickel was immersed in the liquid. In other words, hydrogen was added to the oil. The industry of oil hardening thus began, but with the handicap of a dry-made catalyst. Although simple enough to make in the laboratory, there appeared no end of woes when attempting to prepare this same catalyst on the large scale. When, finally, industry perceived that wet rather than dry reduction was the most fitting solution of liquid phase hydrogenation from the catalyzer standpoint, a substantial economy in operating costs and a great simplification in plant practice was achieved.

1140. This development did not proceed without its disputes of priority. A number of interferences arose in the United States Patent Office. Those between Wimmer and Higgins vs. Ellis and Hausmann vs. Ellis (see para. 1171, footnote 47) resulted in an award of priority to Ellis. Subsequently a four-party interference was declared between Morrison, Granichstaden, Wimmer and Ellis. The interference covered the subject matter, broadly, of producing a metal catalyzer by subjecting a heated mixture of oil and a substantially non-catalytic reducible nickel compound to the action of a reducing gas. The parties Morrison and Granichstaden were dropped from the interference, since their dates of conception of the subject matter were subsequent to the date of filing of Wimmer. An appellate tribunal finally held that Ellis was the prior inventor and the broad claims were granted to him. Patents have now been granted on all the applications involved in this interference as follows: H. J. Morrison (assignor to The Hydrogenation Company), 1,299,004, Apr. 1, 1919; E. Granichstaden, 1,314,642, Sept. 2, 1919 (later assigned to Chemical Foundation); C. Ellis, 1,369,013, Feb. 22, 1921; K. Wimmer (assignor to Hydrogenated Oil Company), 1,416,249, May 16, 1922.

1141. Crystalline Nickel Catalyst for Low Temperature Operation. An editorial in the *Journal of the Society of Chemical Industry*, June 24, 1927, describes a method of producing a nickel catalyst active at low temperatures.¹⁶ The special virtue of this catalyst is said to be due to its crystalline form and this is produced by extremely slow precipitation of the carbonate. The carrier (e.g., silica gel powder) is suspended in a dilute solution of nickel nitrate and a very dilute solution of sodium carbonate is added drop by drop during a period of eight hours, the liquid being maintained at 70° C. The precipitate on the carrier after filtration, washing and drying is heated slowly in hydrogen to 420° C. This new catalyst is so active that it gives a 95 per cent yield of isopropyl alcohol from acetone at 40°–70° C. It is hoped that the iso-oleic acid avoidance problem may be solved by the use of this catalyst in the oil hardening industry. Highly active catalysts are, however, usually excessively sensitive to poisons.¹⁷

1142. Precipitation of Catalytic Metals by More Electropositive Metals. Nickel, copper and cobalt are precipitated in a condition suitable for catalysis by addition of iron, zinc or aluminum, to the aqueous solution of salts. This may be done in presence of a non-metallic carrier. If the solution is alkaline the oxide of the electropositive metal is precipitated with the nickel, cobalt or copper and this, in some instances may act as a promoter. Catalysts so prepared may be used for the hydrogenation of organic compounds.¹⁸

¹⁶ U. S. Pat. 1,695,666, Dec. 18, 1928, to Schirmacher, Stolz, Schlichenmaier and Krohs: assigned to the I. G. Farbenind. A.-G.

¹⁷ Cf. Brit. Pat. 255,884 and Swiss Pat. 127,157, July 20, 1926; *Chem. Abst.*, 1929, **23**, 1227.

¹⁸ Brit. Pat. 281,218, Nov. 27, 1926, to I. G. Farbenind. A.-G. Cf. U. S. Pat. 1,451,113, 1923, to Richter.

1143. The precipitation of catalytic metal (e.g., nickel) by means of a more electropositive metal (e.g., zinc or aluminum) in presence of an organic base or acid amide is used to prepare hydrogenation catalysts. Hydrogen may be used preferably with a metal. Inert carriers may be present.¹⁹ Thus nickel chloride is dissolved in water and mixed with ammonium chloride and strong ammonia. Diatomaceous earth and aluminum powder are stirred in, causing the nickel to be reduced. Other bases available are: urea, aniline, toluidine, pyridine, methylamine, piperidine, and hexahydro aniline.

1144. Catalytic Metal Precipitated by Lower Oxide of Silicon.²⁰ Catalysts for hydrogenation may be prepared by reducing metals from their salt solutions by silicon-oxygen compounds of a lower degree of oxidation than SiO_2 , at low or moderate temperatures. Such a catalyst, made from nickel acetate, is suitable for the reduction of nitrobenzene to aniline, nitro-naphthalene to amino-naphthalene, crotonaldehyde to *n*-butylaldehyde, cinnamic aldehyde to hydrocinnamic aldehyde, oleic acid ester to stearic ester and others. Zinc, gold, tin, silver, cobalt, lead, thallium, bismuth, osmium, iridium, copper, platinum and palladium catalysts are made in a similar manner.²¹

1145. Metal Catalysts Precipitated by Hydrogen under Pressure.²² Metallic catalysts such as nickel, cobalt, and copper, or mixtures of these, may be made by precipitation from their ammoniacal solutions by the action of hydrogen or a gas containing hydrogen, under pressure, in the presence or absence of a carrier. The precipitation may be accelerated by the presence on the carrier of a metal having a catalytic action such as nickel, cobalt, or copper.

1146. Metallic Catalysts Made under Pressure.²³ Metallic catalysts may be prepared at low temperatures by the combined use of a catalyst and high pressure. Finely divided metals are obtained by reducing an oxide, hydrate, or salt, with hydrogen in presence of a catalyst at a low temperature. Thus a mixture of kieselguhr with precipitated salts of copper, nickel, or cobalt is heated with hydrogen to 40°–100° C., under a pressure of 20 to 40 atmospheres.²⁴

1147. Working under high hydrogen pressure and at high temperatures Ipatiev reduced metals from their salts in aqueous solution.²⁵

1148. Nickel Metaborate a Catalyst. Schoenfeld²⁶ states that nickel borate heated to 300° C. in an atmosphere of hydrogen loses water and becomes nickel metaborate. This product is a gray substance and is an active catalyst. The analytical figures are held by Schoenfeld to prove the composition. Other workers dispute this conclusion and consider that the so-called "metaborate" is a

¹⁹ Brit. Pat. 286,123, May 6, 1927, to the I. G.; *Chem. Age* (London), 1928, 18, 304; Swiss Pat. 127,516, Mar. 26, 1927, to the I. G.; *Chem. Abst.*, 1929, 23, 1226.

²⁰ Brit. Pat. 301,577 to Imray (from I. G. Farbenind. A.-G.), Sept. 19, 1927, French Pat. 641,652, Sept. 29, 1927, to I. G.

²¹ The silicon compound to which reference is specifically made is known as "oxydisilin" (*Brit. Chem. Abst.*, 1929, 122B).

²² Brit. Pat. 282,410, Dec. 14, 1927, addition to 281,218, to I. G. *J.S.C.I. Suppl.*, June 22, 1928, 452.

²³ Brit. Pat. application 293,749, by I. G. (convention date July 11, 1927).

²⁴ *Chem. Age* (London), 1928, 19, 243.

²⁵ *J. Russ. Phys. Chem. Soc.*, 1909, 41, 769; *Chem. Abst.*, 1910, 4, 7.

²⁶ *Seifen. Ztg.*, 1914, 945.

mixture containing metallic nickel, boron oxides, etc. Normann²⁷ claims to have demonstrated the presence of metallic nickel. Working with Rack, Erdmann²⁸ characteristically discovers the suboxide and attributes to it the catalytic activity observed by Schoenfeld.

1149. In Ellis's laboratory nickel sulphate solution was treated with sodium metaborate. The precipitate was dried at 100° C. and dehydrated in hydrogen at a higher temperature. The product was found to give results in the hydrogenation of cottonseed oil as reported by Schoenfeld.

1150. In describing a hydrogenation catalyst made of a nickel salt of an inorganic acid not volatile at the temperature of hydrogenation, the significant remark is made that it is preferable to heat the catalyst in a current of hydrogen before use.²⁹

1151. Normann³⁰ refers to hydrogenation by means of organic nickel salts such as the formate, acetate, stearate and oleate as only a special case of use of metallic nickel catalyst since formation of the metal always occurs before hardening takes place.³¹ In fact, the liberation of organic acids in a state of purity is secured in many cases by passing hydrogen into the corresponding salt of nickel,³² affording a technical process for the preparation of pure concentrated organic acids. It also is known that inorganic salts of nickel can be reduced by hydrogen to the metallic state,³³ and that catalysts have been prepared by the reduction of inorganic nickel salts.³⁴ It is to be expected that nickel borate would be broken down to a greater or less degree into metallic nickel and free boric acid on heating in a stream of hydrogen. This decomposition actually occurs, yet when reduction takes place below 300° but very little boron trioxide volatilizes. On heating nickel borate in an electric furnace at 300° in a current of air, some boric acid sublimes and the borate turns to a deeper shade of green. Water hydrolyzes the borate, forming free boric acid and nickel hydroxide. Nickel borate was heated in a current of hydrogen for one-half to three-quarters of an hour at temperatures ranging from 300° to 400° C. The product reduced at 300° was used to hydrogenate cottonseed oil and in three hours' treatment at 170° to 180° C. the iodine number was reduced from 108 to 104.5. By reduction of the borate at 350° an iodine number of 101.4 was obtained under otherwise similar conditions. The borate reduced at 400° was considerably darker in color, and cotton oil treated with it exhibited an iodine number of 47.7. No hydrogenation of the oil was perceptible when using nickel borate without previous reduction.

1152. In order to show the presence of free metallic nickel in this borate catalyst the carbon monoxide method³⁴ was applied. It was found that free boric acid prevented the reaction between carbon monoxide and nickel. Accordingly the reduced and cooled borate was introduced into water (in an atmosphere of carbon dioxide to prevent contact with oxygen), the mixture warmed on the water-bath and filtered in such a manner as to avoid contact with air. The precipitate, thus freed of boric acid, was dried in hydrogen below 100° C., and after drying was exposed to carbon monoxide. The gaseous products of reaction were passed through a heated tube of glass and the rate of formation of a nickel mirror noted. The borate reduced at 300° and 350° quickly yielded a slight but distinct nickel mirror, while the product reduced at 400° formed a heavy mirror. This is considered proof of the presence of metallic nickel in the reduced borate and the former only is responsible for hydrogenation.³⁵

1153. The catalytic activity of the compound was determined in the following simple manner: One hundred to 200 g. of the oil with 1 per cent of the nickel borate were placed in a flask of about $\frac{1}{2}$ -liter capacity and were heated to 160° to 180° C., while hydrogen was passed through the oil. After the hydrogen was introduced in this manner for a short time the con-

²⁷ *Seifen. Ztg.*, 1915, 46-47.

²⁸ *Seifen. Ztg.*, 1915, 3.

²⁹ French Pat. 470,364, Mar. 28, 1914; Swed. Pat. 41,331, Sept. 13, 1916, to G. Müller Speisefettfabrik A.-G.; cf. Brit. Pat. 148,111, July 8, 1920; *Chem. Abst.*, 1921, 185.

³⁰ *Seifen. Ztg.*, 1915, 46-47.

³¹ Meigen and Bartels, *Journ. prakt. Chem.*, 1914, 89, 290.

³² Ger. Pat. 217,846.

³³ Gmelin-Kraut V, 1, 23, 1909.

³⁴ *Journ. of Gas Light*, 1, 7, 13, page 31.

³⁵ *Chem. Ztg.*, 1915, No. 6 and No. 7/8.

³⁶ See also Normann and Schick, *Arch. Pharm.*, 1914, 252, 208.

tents of the flask acquired a grayish color as the result of the fine distribution of the catalyzer in the oil. Hydrogen was applied for two and one-half to three hours and the oil then filtered through paper. The residue of the catalyzer was extracted with ether and benzene until supposedly free from oil, but on treatment with dilute mineral acids, oily drops separated. It was, therefore, concluded that during the hardening some of the free fatty acid present in the oil combined with nickel, forming a metallic soap with liberation of boric acid. To ascertain if this were the case 5 g. of the used catalyzer were dissolved in dilute hydrochloric acid and the oil which separated was extracted with ether and purified. The oil obtained was yellowish in color and contained about 50 per cent of free fatty acid corresponding to an acid number of 98. The acid number of the original oil was 0.3. After the hardening operation the nickel borate was found to contain less boric acid than corresponded to the original formula.

ANALYSIS OF NICKEL BORATE USED FOR HARDENING

	NiO	B ₂ O ₃
1. Used once.....	42.07	28.3
2. Used twice.....	44.3	33.84
3. (a) Used once.....	43.5	34.9
(b) Used twice.....	43.88	33.5
(c) Used three times.....	45.5	29.42

In experiment (3) an endeavor was made, by careful drying of the hydrogen, to reduce the formation of fatty acid to a minimum. The same mass of catalyzer was used four to six times for hardening without any diminution of its activity. From the following observations Schoenfeld concluded that catalysis was due to nickel borate alone and not to the small amount of nickel soap present for the reason that (1) the temperature of 160° to 180° was regarded as insufficient to cause nickel soap to become active; (2) the amount of the latter was too slight to effect any considerable change, and (3) if the nickel soap were responsible for hydrogen addition the activity of the nickel borate catalyzer would increase with repeated use as a result of the increase in the amount of nickel soap. Schoenfeld found that as the content of nickel borate is reduced the activity of the catalyzer correspondingly diminishes. Various oils were treated with the borate catalyzer, including cottonseed, rape, linseed, soya-bean and whale oil, and satisfactorily hardened products obtained. In one experiment made by Schoenfeld 200 g. of cottonseed oil were mixed with 2 g. of nickel borate and heated for three hours at 160 to 170° in a stream of hydrogen. The solidifying-point of the hardened oil was 38° C. By longer action of the hydrogen a solidifying point of 47° was obtained. The application of pressures of $\frac{1}{2}$ to 1 atmosphere somewhat improved the reaction so that in two hours linseed oil, for example, was converted into a fat of the consistency of tallow with a solidifying-point of 38°. The hardened oils which Schoenfeld prepared by means of nickel borate possessed a pure white color and the acid number was not increased by the hardening treatment. Schoenfeld regards nickel borate especially desirable as a catalyzer because it appears that the ordinary catalyzer poisons such as sulphur do not affect the activity of the borate. Schoenfeld in fact added sulphur to cottonseed oil and claims no detrimental effect was incurred thereby. He summarizes the advantages of using nickel borate, as follows: The hardening occurs at a relatively low temperature (160° to 180° and in most cases between 160° to 170°). The application of gas under pressure is not necessary, and the hydrogenation can be carried out in very simple apparatus. The lack of sensitiveness to catalyzer poisons and the ability to use the nickel borate repeatedly also are advantages.

1184. Erdmann and Rack³⁷ carried out various tests with nickel borate which led them to regard Schoenfeld's conclusions as unreliable. It was noted that Schoenfeld used Kahlbaum's nickel borate containing slightly more nickel than corresponded to the formula NiO·B₂O₃ on linseed oil and also on the easiest of all fatty oils to harden, i.e., refined cotton oil. No hydrogenating action was observed with either hydrated or anhydrous nickel borate at a temperature of 175° C. Green nickel borate was heated for one-half hour at 330° to 340° C., in a stream of nitrogen. Four grams of this borate material was introduced into 400 g. of cotton oil which previously had been heated to 100° C. The temperature was raised

³⁷ *Seifen. Ztg.*, 1915, 3.

to 175° C. and a stream of hydrogen at the rate of 20 liters per minute was passed through the oil for three hours. No hardening occurred. Linseed oil gave the same results. Green nickel borate was heated in hydrogen at 300° to 305° C. for one-half hour, and during this treatment the color of the material changed from yellowish-brown to gray. An aqueous solution of phosphomolybdic acid was colored blue on standing with some of the gray product. Cotton oil treated for nine and one-half hours with this hydrogen-treated material hydrogenated only slightly, indicating very weak hydrogenating power.

1155. A quantity of the borate was exposed to hydrogen at a temperature of 340° and a dark gray product obtained. Under the same conditions except in an atmosphere of nitrogen a yellowish-brown material resulted. While the latter material was neither magnetic nor reactive with phosphomolybdic acid, the dark gray product was attracted by a magnet and colored phosphomolybdic acid strongly blue. Some of the gray product was pressed to form a block and a current of electricity at 80 volts used to test its electrical conductivity. No passage of the current could be detected when employing a sensitive milliammeter, from which Erdmann concluded that no metallic nickel, but nickel suboxide, was present. On treatment with dilute mineral acid hydrogen was evolved in an amount corresponding to 7.4 per cent nickel suboxide (Ni_2O_3).

1156. Four grams of the dark-gray product were mixed with 400 gs. of edible cotton oil and on heating to 175° to 180° C., a hydrogen stream (20 liters per minute) was passed through the oil for three hours when the solidifying-point of the latter was found to be 31.8° C. The catalyzer distributed well through the oil in the manner characteristic of nickel suboxide and due, it is stated, to the formation of an organosol. The recovered catalytic agent did not exhibit any electrical conductivity. Five hundred grams of cotton oil were heated to 125° C., 15 g. green nickel borate were added and the temperature was then raised to 260°. A stream of hydrogen was passed through the oil for five hours, and the oil was found to be hydrogenated to a solidifying-point of 31.8°.

1157. As is known, boric acid is a very weak acid body and the salts of mono- and tri-basic boric acid are, therefore, very unstable. Salts of the nature of borax derived from tetra boric acid are more stable. On heating nickel borate $\text{NiO} \cdot \text{B}_2\text{O}_3$ to 300° it is likely that nickel oxide and tetra borate form according to the equation $2\text{NiB}_2\text{O}_4 = \text{NiB}_4\text{O}_7 + \text{NiO}$. By treatment with hydrogen for one-half hour at 300° or even at 340° C., nickel suboxide, not metallic nickel is stated to be formed. While pure nickel oxide is readily reduced to the metallic state by hydrogen at 300° C., this is held not to occur in the presence of boric acid, which acts to retard reduction. This acid belongs to a class of bodies which so hold back the reducing reaction that either resort must be had to higher temperatures to secure the metal, or the intermediate suboxide phase obtains according to circumstances.

1158. Summary. 1. Neither hydrated nor anhydrous nickel borate has proved active as a fat-hardening catalyst at a temperature of 175° C.

2. By heating nickel borate in hydrogen at 300° to 340° C., a partial reduction to the suboxide of the nickel oxide present in the borate occurs. Due to the presence of the suboxide, the material subdivides in fatty oils and acts catalytically at 175° although less effectively than pure nickel suboxide.

3. If a fatty oil is heated with green nickel borate to 260° C., and treated with hydrogen, decomposition occurs with formation of nickel oxide and suboxide, and these products act as hydrogen carriers in the same manner as the decomposition products of organic nickel salts such as nickel acetate have been observed to function.²⁸ It is claimed by Erdmann and Rack that Schoenfeld is in error in ascribing the hydrogenation of fats when using nickel formate, acetate, etc., to the agency of metallic nickel, as nickel oxides are considered responsible for the reaction.

4. No advantages over nickel oxide have been found in nickel borate. The low temperature of hardening observed with the latter is merely a consequence of the prior formation of nickel suboxide. The property of the latter to act as a hydrogen carrier at a temperature below 200° C., was already known. The advantages ascribed to nickel borate by Schoenfeld, namely, that no hydrogen pressure above atmospheric is required, hence the hydrogenation process may be carried out in very simple apparatus, the slight degree of sensibility to catalyzer poisons, the ease of separation of the hardened product from the catalyzer, the ability to use the catalyzer repeatedly, are all features of value applicable to the nickel oxide process as pointed out in Ger. Pat. No. 266,438 and elsewhere. Nickel borate possesses the practical disadvantage that it affords nickel oxide loaded with material of no value in the hardening process.

²⁸ *Journ. prakt. Chem. (N. F.)*, **87**, 449 and 452. For the question of nickel suboxide see Chapter XII.

1159. Schoenfeld³⁹ discusses the observations of Bosshard and Fischli⁴⁰ who, Schoenfeld notes, on the basis of an experiment with oleic acid, have stated that in the hydrogenation of oils in presence of nickel borate, catalytic action comes into play only after the borate is decomposed.

1160. Schoenfeld points out that his conclusions in regard to the favorable action of nickel borate as catalyst referred only to neutral fats and that he was aware of the decomposition of nickel borate by free fatty acids. In Bosshard and Fischli's experiment, the activity diminished with increasing decomposition of the catalyst, and this confirms Schoenfeld's contention that nickel borate is a more effective hydrogen carrier than the mixture of nickel and nickel oxide (with boric acid) formed by its decomposition. In many cases hardened fats (especially from marine animal oils) produced with the aid of nickel or nickel oxide contain more nickel than those prepared with the aid of nickel borate. Schoenfeld disputes the statement of Bosshard and Fischli that the catalytic hydrogenation of oils in presence of nickel borate is conditioned by the previous decomposition of the salt; the reverse, in fact, he claims is the case, for with increasing decomposition of the borate owing to the action of the free oleic acid used in Bosshard's experiment, the activity of the catalyst diminishes. The relatively high nickel content of the oleic acid hardened in presence of nickel borate is likewise to be attributed by Schoenfeld to the decomposition of the salt by the free fatty acid.

1161. **Preparation of Catalysts by Thermal Reduction of Nickel Salts.** Some nickel salts will decompose on heating, liberating free metal. This phenomenon is most often exhibited by organic compounds, notably the formate. Solutions of nickel hypophosphite, however, decompose in this way on boiling.

1162. The production of catalytic nickel by thermal decomposition of organic salts may be effected: 1. By dry heating, e.g., nickel formate heated 10° C. above initial temperature of decomposition.⁴¹ 2. By heating in an oily or waxy medium.⁴² Formate, stearate, acetate, oleates, etc., heated in oil, to about 250° C. (with or without hydrogen), *in vacuo*.⁴³

1163. But slightly different from the processes using straight thermal decomposition of such salts as the formate are those which combine heating with the use of a reducing gas such as hydrogen.

1164. **Hydrogenation with Formate Alone.** Higgins⁴⁴ effects the reduction of unsaturated compounds in the presence of a metallic formate, without employing gaseous hydrogen.

1165. In carrying the method into effect in its application to unsaturated fatty acids or their esters, these bodies are intimately mixed with the salt of formic acid and a catalytic substance and the mixture is placed in a vessel capable of being rendered gas-tight and provided with an agitator. The contained air is preferably exhausted from the vessel or displaced by a non-oxidizing gas, such as carbon monoxide, nitrogen, carbon dioxide, or hydrogen and the temperature then carefully raised when the reaction takes place, which may, for example, be represented thus:



1166. The end-products vary with the formate used, that is, with some formates, the resulting metallic carbonate is unstable and carbon dioxide is evolved as well as carbon monoxide. Owing to the evolution of carbon dioxide or carbon monoxide, or both, considerable pressures are generated.

1167. Higgins suggests the following:

1. Nickel formate as the reducing agent and the catalyst. 2. Zinc formate as the reducing agent together with a known catalyst. 3. Zinc formate as the reducing agent

³⁹ *Z. angew. Chem.* 1916, **29**, 39; *J.S.C.I.*, 1916, 367; *J. Chem. Soc.*, **110**, 1, 248.

⁴⁰ *J.S.C.I.*, 1915, 1079.

⁴¹ U. S. Pat. 1,390,685 to Ellis.

⁴² U. S. Pats. to Ellis, 1,378,336, 1,378,337, 1,378,338.

⁴³ U. S. Pat. to Ellis, 1,390,683, specifies heating in paraffin.

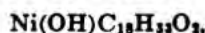
⁴⁴ U. S. Pat. 1,170,814, Feb. 8, 1916.

admixed with palladium chloride which under the conditions of working is converted into a catalytic substance by the action of the zinc formate.

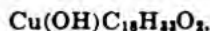
The heating must be conducted with care, as local superheating may cause spontaneous formation of oxalate from the formate and is liable to produce explosion. For this reason the apparatus must be provided with necessary safety devices. The reaction can be conducted practically quantitatively, but for commercial purposes an excess of the reagent over the theoretical amount necessary is preferably employed. The materials taking part in the action should be dry. The temperature may vary with the formate or mixture of formates or other reagents employed, but in general may be in the neighborhood of 20° below the point at which the formate used, spontaneously decomposes to the oxalate under the pressure existing in the apparatus at the time of so heating.

1168. Soap Catalysts. According to Hausmann⁴⁵ effective hydrogenation of unsaturated substances is obtained by the use of a basic compound of a suitable metal (for example, copper, nickel, cobalt, and other non-noble metals), with a fatty acid soluble in the fatty compound to be treated, such, for example, as oleic, stearic, or like acid. These metallic soaps dissolve in the melted fats or oils, and, on passing hydrogen through the mixture (at a temperature between 100° and 180° C.) a colloidal metallic hydride is formed that is regarded as the active agent in the reducing or hydrogenating reaction. The hydride exists in the mixture as long as there is free hydrogen present. Small additions of such a metallic soap are sufficient to reduce large quantities of the unsaturated materials. The same fatty acids as exist (usually as glycerides) in the compounds to be treated are preferably employed to form the basic metallic compound used for catalysis. The conversion of the basic metallic compound into an active catalyzer, when dissolved in the fatty material, takes place gradually in the hydrogen atmosphere at temperatures above 100° C. and a temperature of from 160° to 180° C. is recommended in practice. At this temperature copper or other hydride is obtained in colloidal condition.

1169. As an example of the process the following may be taken: 500 parts by weight of raw soya-bean oil are mixed with 0.4 per cent of the basic oleate of nickel:

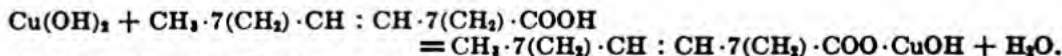


and the mixture is exposed at about 160° C. to the action of hydrogen by any of the well-known methods until the desired degree of hardening is attained. In using a basic oleate of copper



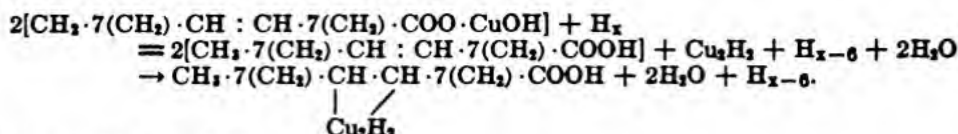
dissolved in the fat and uniformly distributed throughout the whole mass, the compound is acted upon by hydrogen with the formation of water and the mass becomes dark brown. At this stage the freed hydroxyl group probably plays a part in the formation of a copper hydride. By alternate formation and decomposition of this colloidal copper hydride the hydrogen is rendered active, converting the unsaturated fatty compounds into saturated, for instance the oleic acid into stearic acid. Analogous reactions occur with the various other metallic compounds which may be employed. In no case is the metal itself produced or its oxide, as in some of the prior processes, except at the end of the reaction, when free hydrogen is eliminated to gradually decompose the hydride.

1170. The reactions which occur may be given approximately by the following equations: Formation of the primary catalyst



that is, basic copper oleate.

The reaction of this oleate with hydrogen



The resulting products are



⁴⁵ U. S. Pat. 1,145,480, July 6, 1915, Canada, 157,396, Aug. 18, 1914.

1171. The application of nickel oleate in hydrogenating oils, as described by Ellis,⁴⁶ involves, in one form, the thermal decomposition of the oleate in an oily vehicle. Besides nickel oleate any suitable metallo-organic compound, especially one soluble in oil and consisting of a metal united to a weak organic acid may be used as a source of catalytic material.^{47, 48}

1172. By heating these metallo-organic compounds decomposition occurs setting free the catalytic material in a state of extreme subdivision and sometimes forming a colloidal solution. When the catalyst has been prepared in this manner, it is admixed with the oil that is to be hydrogenated and hydrogen is introduced. In those cases where the metallic catalyst tends to dissolve in an acid fatty body to form a metallic soap, the temperature during hydrogenation may be maintained at a point above that at which the soap is unable to exist, or if previously formed may be decomposed. A temperature of about 10° above the decomposition point is recommended.

1173. Details of preparation of catalysts by the thermal decomposition of nickel oleate or other organic compound of nickel are indicated by Ellis.⁴⁹ A catalyst may be made by the reduction of nickel acetate in hydrogen.⁵⁰ A mixture of nickel formate and nitrate when heated gives catalytic nickel material.⁵¹ Ellis proposes to make a catalyst concentrate by decomposing in oil, an excess of a decomposable compound of nickel.⁵² Nickel carbonyl may be used in this case.

1174. Nickel Catalyst from Sulphate and Formate. According to Ellis, a catalyst suitable for hydrogenating oils is prepared by mixing solutions containing equivalent proportions of nickel sulphate and calcium formate (or other soluble formate), evaporating to dryness, and heating the dried product to about 240° C. If the temperature does not exceed 250° C. no sulphides or other catalyst poisons are formed, while the presence of the sulphate is advantageous in the hydrogenation.⁵³

1175. Nickel Catalyst from Hypophosphite. When nickel hypophosphite solution is boiled, metallic nickel is precipitated, under some conditions as thin metallic leaves, under other conditions as a fine powder. The latter form acts catalytically on sodium hypophosphite in solution giving acid sodium phosphite with evolution of hydrogen. The powder form is obtained by dissolving 20 g. nickel sulphate in 100 cc. water, heating on a water bath, introducing in one addition 70 g. sodium hypophosphite and stirring. At the end of one hour reduction is complete. Distilled water is added, the nickel material is allowed to settle and is washed by decantation. Palladium prepared in a somewhat similar manner decomposes sodium hypophosphite very effectively.⁵⁴ Ellis has noted that this precipitated nickel material is catalytic and readily acts to harden cottonseed oil at a temperature of 210° C., or thereabouts, with hydrogen at atmospheric pressure.

⁴⁶ U. S. Pat. 1,217,118, Feb. 20, 1917.

⁴⁷ Patent No. 1,217,118 was involved in an interference with the Wimmer and Higgins Patent No. 1,081,182 and priority was awarded to Ellis for this use of organic compounds of nickel in the hydrogenation process.

⁴⁸ In an interference with Hausamann, priority was also awarded to Ellis and the application on which Letters Patent No. 1,145,480 was issued to Hausamann July 6, 1915, was involved in a like interference. See para. 1140.

⁴⁹ U. S. Pat. 1,251,201, Dec. 25, 1917.

⁵⁰ Ellis, U. S. Pat. 1,251,203, Dec. 25, 1917.

⁵¹ U. S. Pat. 1,251,204, Dec. 25, 1917, to Ellis.

⁵² U. S. Pat. 1,251,202, Dec. 25, 1917.

⁵³ U. S. Pat. 1,482,740, Feb. 5, 1924.

⁵⁴ Breteau, *Bull. Soc. Chim.* (1911), 9, 515-519.

1176. Nickel Compounds Reduced by Ignition with Carbonaceous Material.

In one of the earliest descriptions of the production of a nickel catalyst by this method ⁵⁵ nitrate of a catalytic metal (e.g., nickel) is directed to be heated with an organic compound (e.g., sugar). The resulting voluminous product is reduced by hydrogen at 200°–300°, yielding an active metal powder.⁵⁶

1177–1178. Patents taken out by Schuck ⁵⁷ and by Baker ⁵⁸ developed this method. A solution of the nitrate and of sugar (e.g., 0.1716 nickel nitrate, 0.25 sugar per cubic centimeter of water) is atomized by inert gases through a muffle at 550°–650° C. The product is black, flaky and non-pyrophoric: it is removed by suction while still suspended in the inert gases.⁵⁹

1179. In 1916 Arldt ⁶⁰ described a catalyst made by mixing metal, or reduced metallic compound with sugar and carbonizing the mixture with sulphuric acid. The process is said to be applicable to the regeneration of catalyst poisoned by organic residues.

1180. Valpy and Lucas⁶¹ described the preparation of metallic catalysts by the ignition of oxalates, tartrates and acetates of nickel and iron. In 1923 they published a process ⁶² for the preparation of catalysts by mixing ground metallic oxides, such as those of iron, nickel or manganese, and organic compounds of metals, e.g., acetates or tartrates, with a carbonaceous reducing and binding material, such as tar, heating until oxides of carbon are given off, regrounding coarsely, mixing with a second quantity of carbonaceous material and, finally, heating to a considerably higher temperature, so as to reduce the metal completely and to produce a porous *sintered* mass.⁶³

1181. The Valpy and Lucas catalysts are usually composed of more than one metal and they are intended, especially, for use in the cracking of hydrocarbon oils.

1182. Thomas ⁶⁴ in the investigation of the relative activities of nickel catalysts prepared in different ways, did not make experiments on all fours with the methods of preparing catalysts by ignition of nickel compounds with carbonaceous material, such as we have just been considering. He did, however, prepare a catalyst by mixing nickel oxide on kieselguhr with sugar charcoal and heating in a current of nitrogen to exclude air.

In these conditions reduction to the extent of about 85 per cent occurred at 600° C., but complete reduction was not easily attained. At 650° C. reduction to metallic nickel was almost complete in one and one-half hours. A comparison of the activities of catalysts obtained in this way with the one obtained by the standard method (a) was carried out by noticing the comparative falls in iodine absorption on bubbling hydrogen through cottonseed oil at 180° C. in the presence of 0.5 per cent of nickel, with the following results:

⁵⁵ Oelwertung G.m.b.H., Italian Pat. 130,394, Mar. 13, 1913.

⁵⁶ Cf. Austr. Pat. 70,930, Jan. 10, 1916; *Chem. Abst.*, 1916, 1279.

⁵⁷ Brit. Pat. 142,576, Feb. 18, 1919; U. S. Pat. 1,305,173, May 27, 1919; Canadian Pat. 200,591, June 1, 1920; U. S. Pat. 1,467,397, Sept. 11, 1923.

⁵⁸ Brit. Pat. 222,922, July 3, 1923.

⁵⁹ In Brit. Pat. 142,576 it is said to contain nickel but no carbon; in Canadian Pat. 204,612 it is said to be a suboxide (*Chem. Abst.*, 1920, 3768); in U. S. Pat. 1,305,173 the product is described as an uncoked mixture of nickel and carbon. Baker's patent and Schuck's U. S. Pat. 1,467,397 deal with the apparatus for carrying out the process and, more particularly, with the controlled feed valves for the inert gases.

⁶⁰ D.R.P. 356,614, Apr. 23, 1916; *J.S.C.I.*, 1922, 41, 770A.

⁶¹ Brit. Pat. 5,847, 1914.

⁶² Brit. Pat. 209,355, Apr. 26, 1923, to V. L. Oil Processes, Ltd., with O. D. Lucas.

⁶³ Also U. S. Pat. 1,502,260, July 27, 1924, to O. D. Lucas.

⁶⁴ *Loc. cit.*

	Time of Hydrogenation	Iodine Absorption of Oil
Original oil	111.0
(a) Ni reduced in hydrogen at 350° C.	90 min.	61.0
(b) Ni reduced by charcoal at 600° C.	180 min.	86.8
(c) Ni reduced by charcoal at 650° C.	180 min.	101.6

1183. Thus a nickel catalyst prepared by reduction with charcoal at 600° is about one-third as active as a catalyst reduced by hydrogen at 350° C., while reduction at 650° C. gave an almost inactive product.

1184. Preparation of Catalyst by Heating Metallic Salt with Wax or Oil to Cracking Temperature. This method is described by Ellis⁶⁵ as a means for making powdered metals and reduced metallic compounds, and catalyst for oil hardening. Metallic compounds not reducible by heating in oil, in the absence of reducing gases, may be reduced by heating in a suitable vehicle to the cracking point of the latter, without the production of tars. As catalyst material compounds of nickel or other metals whose atomic weights are approximately between 58.7 and 63.6 may be used: special mention is made of nickel carbonate, of basic nickel salts, and of inorganic salts not reducible by heat alone to metal. The temperature specified is the cracking point, generally between 300° and 340°. Important working points are agitation, concentration of product, and avoidance of tar formation by temperature control. The product is defined as a catalyst compound of reduced metal of atomic weight between 58.7 and 63.6, or reduced nickel powder of black color suspended in the cracked vehicle.

1185. Rapid Determination of Nickel. Spacu and Dick⁶⁶ recommend the following procedure: 100 cc. of nickel solution are treated with 0.5 g. of ammonium thiocyanate for every 0.1 g. of nickel present, heated to boiling, and treated drop by drop with 1–2 cc. of pyridine. After cooling completely, the precipitate of glistening, sky-blue prisms is collected on a filtering crucible and washed successively with water containing 4 g. of ammonium thiocyanate and 6 cc. of pyridine per liter, 35 per cent alcohol containing 15 cc. of pyridine and 1 g. of ammonium thiocyanate per liter, absolute alcohol containing 5 cc. of pyridine per 100 cc., and ether, to 20 cc. of which are added 2 drops of pyridine. The crucible and contents are dried in a vacuum desiccator for ten minutes and weighed. The compound, $\text{Ni}(\text{SCN})_2 \cdot 4\text{C}_2\text{H}_5\text{N}$, contains 11.95 per cent nickel.⁶⁷

RELEVANT REFERENCES

1186. Hatschek and Thorne. Metal sols in non-dissociating dispersion media. *Kolloid Zeit.*, 1923, **33**; 1925, **36**, 1925.

1187. Tammann and Nikitin. Pyrophoric properties of metal powders *Z. anorg. Chem.*, 1924, **135**, 201.

1188. Tammann and Marais. Reduction of thin films of oxide on copper and nickel. *Z. anorg. Chem.*, 1925, **135**, 127.

⁶⁵ U. S. Pats. 1,329,322, and 1,329,323, Jan. 27, 1920; Canadian Pat. 226,305, 1922. The claims are numerous and for details the original should be consulted. In general, the claims cover the use, as vehicle, of any oil or wax capable of being cracked, especially petroleum, wax, paraffin wax, or other solid hydrocarbon or mixtures of these.

⁶⁶ *Z. anal. Chim.*, 1927, **71**, 442.

⁶⁷ *Brit. Chem. Abst.*, 1927, 1047A.

CHAPTER XII

NICKEL OXIDES AS CATALYSTS IN HYDROGENATION

1200. Ipatiev used nickel oxide as catalyst in a large number of high-pressure hydrogenations, and found it preferable to metallic nickel.¹ The facts will more precisely be stated if we say that Ipatiev found that by starting with nickel oxide he got better results than if he used nickel reduced to metal outside the apparatus. He seems to have regarded nickel oxide, or a suboxide produced in the course of his operations, as the real catalyst. This is not a necessary conclusion from his data, and we shall see that there is another and at least equally probable explanation.

1201. In 1910 we begin to hear of nickel oxide as a catalyst in oil hydrogenation and, a little later, of nickel suboxide in the same rôle. To these oxides were attributed several advantages over metallic nickel: they were more active and they were more robust. If they really acted as hydrogenation catalysts, their use possessed the then important advantage of not infringing the basic patents of Leprince and Siveke founded on Normann's work. Inevitably, therefore, patents were applied for and a vigorous polemic started between Erdmann and Bedford, proponents of the nickel oxide catalysts and Normann, who fought against the oxide and for the metal.

1202. When the second edition of this work was published, the nickel oxide controversy was by no means settled. Since that time the results of numerous tests have furnished additional fuel for the fire of argument. The controversy can scarcely be regarded as settled even at the present time although the majority of observers seem to have come to the conclusion that there is no evidence for the existence of a nickel suboxide: that when there is any advantage in the use of nickel oxide in hydrogenation it depends, neither on a hydrogenating activity of the oxide nor on its reduction to a suboxide, but on the condition of the metal when it is reduced from the oxide in such circumstances and, possibly, to a promoter action of nickel oxide.² In view of these pronounced differences of opinion we are, therefore, contenting ourselves with a summary of the controversy in a bibliographic form.

¹ Fokin, *J. Russ. Chem. Soc.*, **1910**, 1074.

² Medsforth, *J.S.C.I.*, 1923, **42**, 423, points out the possibility of nickel oxide acting as a promoter to a nickel catalyst.

SUMMARY IN BIBLIOGRAPHIC FORM OF THE NICKEL SUBOXIDE CATALYST
CONTROVERSY

1203. Bedford and Williams. *J. prakt. Chem.*, 1913, **87**, 425. Nickel oxides are hydrogenation catalysts superior to the metal. Higher oxides become reduced to suboxide; hence improvement with age. Nickel suboxide distinguished from metal by absence of electric conductivity and by non-formation of carbonyl.

1204. Boberg and The Techno.-Chem. Labs., Ltd., Brit. Pat. 4702, 1912. Nickel catalyst containing one or more suboxides made either by controlled reduction or complete reduction followed by controlled re-oxidation.

1205. Erdmann and Bedford. Ger. Pat. 260,009, 1911. Preparation of oxide catalyst, in voluminous form, by ignition of nitrate with sugar.

1206. Bedford and Williams. *J.S.C.I.*, **1914**, 324. Preparation of suboxide of nickel catalyst by heating a mixture of nickel oxide or of an organic salt of nickel with oil in a current of hydrogen.

1207. Erdmann. *Seifen. Ztg.*, **1913**, 605. Oxide catalysts more stable. Colloidal form of suboxide catalyst of great importance.

1208. Mayer. *Seifen. Ztg.*, **1913**, 224. Discusses possibility that oxide catalyst is reduced to metal in operation infringing the basic patent of Leprince and Siveke.

1209. Erdmann. *Seifen. Ztg.*, **1913**, 1325. Discusses the question of the Bedford and Erdmann oxide catalyst and the Leprince and Siveke Ger. Pat. 141,029 (Brit. Pat. 1515, 1903 to Normann).

1210. Moore. *Chem. News*, 1895, **71**, 82. Describes a suboxide of nickel, $\text{Ni}_2\text{O} \cdot 2\text{H}_2\text{O}$.

1211. Bedford and Erdmann. *J. prakt. Chem.*, **1913**, 446. Experimental. Erdmann holds that the reduction to metal does not occur in oil, owing to the latter protecting the oxide. Erdmann prepared Moore's suboxide: it was magnetic, reduced nitric acid, developed hydrogen with mineral acids and formed a good, colloidal hydrogenation catalyst for oils.

1212. *Seifen. Ztg.* **1912**, 1001. Affirmation that oxide catalysts used on large scale have shown no reduction to metal. Cites Ipatiev to same effect.

1213. Sabatier and Espil. *Chem. Ztg.*, **1913**, 1121, and 1549. Studies on quantitative reduction of nickel oxide. At first somewhat inclined to admit existence of Ni_2O ; on further investigation found that careful preparation of oxide leads to complete reduction at 155°C . without suboxide formation.

1214. Sabatier and Espil. *Compt. rend.*, **1914**, 668. Sufficient reduction to metal occurs in oil to explain activity of Bedford-Erdmann "oxide" catalyst. Coefficient of reduction determined.

1215. Bedford and Williams. Brit. Pat. 29,612, 1910. Nickel oxide as oil-hardening catalyst.

1216. Bedford, Williams, Erdmann and Hydroil, Ltd., Brit. Pat. 29,981, 1912. Preparation of saturated fatty acids, glycerides and other esters by use of nickel suboxide. Formula of suboxide undetermined: Müller (*Pogg. Ann.*, 1869, 136, 51) and Glaser (*Ztsch. anorg. Chem.*, **36**, 18) say Ni_2O ; Moore (*Chem. News*, 1895, **71**, 81) says $\text{Ni}_2\text{O} \cdot 2\text{H}_2\text{O}$. Properties of suboxide described as before. According to this patent the making of suboxide precedes the addition to the main body of oil by adding nickel oxide to oil and passing hydrogen at 260°C . till the suboxide is disseminated through the oil as an inky colloidal dispersion.

1217. Bedford and Williams prosecuting application for U. S. Pat. 1,026,339, May 14, 1912, say: "Hitherto nickel oxides have been used as hydrogenation catalysts only at high pressures, quoting Fokin (*J. Russ. Chem. Soc.*, **1910**, 1074) on Ipatiev's work (Ni_2O_3): at high pressures and temperatures better than metallic nickel³; lower oxide participation probable: at lower pressures suboxide forms but hydrogenation does not take place."

1218. Erdmann. *Chem. Ztg.*, **1913**, 1142, 1173 and 1195. Hydrogenation of high-acid fish oil and sulphur-containing cottonseed oils possible with nickel oxide because relatively insensitive to poisons. If process is interrupted before completion it is difficult to remove the oil from the catalyst: when hydrogenation is complete, separation is easy. The used catalyst is a mixture of oxide and suboxide. Bellucci and Corelli believe the suboxide to be Ni_2O (*Atti R. Accad. dei Lincei*, **22**, I, 603 and 703). Erdmann believes that loose addition compound forms between fat and the oxide. Evidence of what appeared to be a nickel carbide found.

³ According to present views there is no such oxide.

1219. Meigen and Bartels. *J. prakt. Chem.*, 1914, **89**, 290. Criticism of Erdmann and Bedford's findings. Nickel oxides are catalytically active in hydrogenation only on reduction to metal. Suboxide formation not confirmed.

1220. Erdmann. *J. prakt. Chem.* Reply to Meigen and Bartels. Says the basic patents (Normann; Leprince and Siveke) based on test-tube experiments. First part of paper taken up with history of the industry. Claims non-use of process from 1902 to 1912 due to inefficiency of metallic catalysts, not to shortage of hydrogen. Long account of experimental work on oil hardening and on tests of used oxide catalysts. Of these relies especially on conductivity tests (made by Tubanat) showing the used catalyst had the resistance characteristic of an oxide, and on carbonyl tests. The used catalyst shows no evidence of carbonyl formation (nickel mirror), while colloidal nickel does.

1221. *Idem.* *J. prakt. Chem.*, 1915, **92**, 390; *Chem. Abst.*, 1916, 1105. Returns to the charge. Affirms that used catalyst does contain metal (evolution of hydrogen, conductivity, carbonyl formation).

1222. Agde (a pupil of Erdmann) wrote a long thesis (Halle, 1914) on the subject of this polemic, based on experimental work on the hydrogenation of chemically pure oleic acid, synthetic triolein, and cottonseed oil freed from aldehydes. He reaffirms Erdmann's position but does not, specifically, meet any of the criticisms on the technique. No new experimental evidence on the existence of a nickel suboxide or on the non-existence of nickel as metal in the used catalyst can be found in this paper, because, apparently, Agde accepted Erdmann's methods of investigation and his interpretation of the results. From this point of view, therefore, this very lengthy thesis contributes nothing to the controversy except that the results obtained with pure substances may be interpreted as even more in favor of Erdmann's views than those obtained with ordinary oils. With ordinary vegetable oils it is admitted that nickel is formed, a reduction attributed to aldehydic impurities. The thesis contains a full discussion of the nickel-fat and nickel carbide complexes mentioned by Erdmann.

1223. Normann. *J.S.C.I.*, 1915, 237, 969; 1916, 262. Erdmann quoted by Agde, *loc. cit.*, having said that reduction of nickel oxide was due to impurities in the oil, Normann mixed 1 g. pure nickel oxide with 100 g. synthetic triolein and hydrogenated at 250° C. Within a few minutes a pronounced carbonyl reaction was obtained and the catalyst was conductive.

1224. Oelwerke Germania. *Seifen. Ztg.*, 1914, 645. By repeated use Erdmann's oxide catalyst becomes more active and can be used at the same temperature as the metal catalyst. At first 250° C. is necessary in order to form free nickel.

1225. Freicha. *Arch. Pharm.*, 1915, **253**, 512; *Chem. Abst.*, 1916, **10**, 441. Existence of suboxide entirely problematical. Failure of Erdmann to get conductivity due to adherence of fat, etc., Siegmund and Suida similarly failed to detect conductivity in a mixture known to contain 48 per cent of metallic nickel. Concludes "No hardening without free metal."

1226. Normann. *Chem. Ztg.*, 1916, **40**, 381; *J.S.C.I.*, 1916, 641. Kieselguhr with 20 per cent of nickel, reduced in hydrogen for an hour at 500° C., showed no conductivity. Kieselguhr mixed with 5 per cent of nickel (reduced from oxide at 280° C.) showed good conductivity.

1227. Siegmund and Suida, *J. prakt. Chem.*, 1915, **442**. This is a far more critical paper than Agde's, indeed than any previous contribution to either side of the polemic. The catalyst which Siegmund and Suida call metallic nickel (and on which they base their comparison of activities) was made by reducing nickel oxide in hydrogen at 280°-290° C. outside the reaction vessel. No precaution seems to have been taken to insure that the reduced material did not undergo oxidation. Siegmund and Suida went to great pains to analyze the product attained by reducing nickel formate by heating in nitrogen, proving that it contained oxygen. It was magnetic and its conductivity was zero; the carbonyl test was negative for metallic nickel. They did not (apparently) subject this catalyst after it had been used to the carbonyl test under rigid conditions. All their used catalysts were magnetic. The catalyst from formate was the best, that which Siegmund and Suida call "metallic nickel" the poorest. Their conclusion is that under ordinary pressure hardening of oil takes place incomparably quicker with nickel "oxide" than with "nickel." (The quotation marks are ours.)

1228. Bedford and Erdmann, U. S. Pat. 1,200,696, 1916. See Ger. Pat. 260,009, previously cited.

1229. Boberg. U. S. Pat. 1,093,377, Apr. 14, 1914. See Brit. Pat. 4702, 1912, previously cited. Boberg states that he has "made experiments with various products of reduction and has obtained the following results: The product of reduction of such a composition that an ultimate analysis gives a proportion of nickel to oxygen corresponding to an imaginary formula $Ni_{1.2}O$, i.e., but little suboxide, produced, in a certain time, hardening of a liquid

fat up to a melting-point of 40° C., whereas, a product corresponding to an imaginary formula $\text{Ni}_{3.44}\text{O}$ gave in the same time and for the same material hardening corresponding to a melting-point of 58° C. It appeared, however, that with a lesser proportion of nickel in the product, i.e., a composition that apparently indicated the presence of higher oxides, the product was less active, while, at the same time, compounds containing even higher proportions of metallic nickel than that first specified above, viz., $\text{Ni}_{3.5}\text{O}$, were still less active than the latter."

1230. Erdmann and Rack. *Seifen. Ztg.*, 1915, 75. Nickel suboxide is formed when nickel borate is heated in oil at 260° C. in a current of hydrogen. The same suboxide is produced by reducing the borate as a dry powder at 340° C. in hydrogen.

1231. In 1915 the discussion turned, also, on the reduction of nickel borate and of organic salts of nickel (e.g., the formate) in oil by a current of hydrogen.

1232. Erdmann. *Seifen. Ztg.*, 1915, 288. No new evidence. Reasserts that positive proof of formation of nickel suboxide is found in the (1) black color resulting from subdivision of the catalyst, (2) the lack of electrical conductivity of the used *fat-free* catalyst.

1233. Normann. *Seifen. Ztg.*, 1915, 47 and 191. Blackening of oil does not prove suboxide formation: finely divided nickel (e.g., when carbonyl decomposes in oil) is black.

1234. Normann and Pungs. *Chem. Ztg.*, 1915, 29. Criticize technique of Bedford and Erdmann in looking for metallic nickel. They report their own results on used oxide catalysts. When coefficient of reduction is poor so also is the conductivity, the longer the use the higher the conductivity till it reaches a maximum at 41 per cent free nickel. In one example when the iodine number of the (cottonseed) oil was still 63, the conductivity was nil, when the iodine number had fallen to 3.85 the conductivity was good. The used "oxide" catalyst was in part magnetic, which made possible a fractionation of metal from oxide. Moore's "suboxide" is a non-conductor, but after use as a catalyst in oil it showed excellent conductivity. The carbonyl test requires rigid technique; when this is used Erdmann's "oxide" catalyst after use gives a positive result (nickel mirror).

1235. Nickel Carbonyl Test for Free Nickel. As this carbonyl test has its own importance, apart from the particular controversy in which Normann was engaged we give details of the method. The greatest care should be taken to have the carbon monoxide employed very pure and thoroughly dry. Normann and Pungs prepared the monoxide by allowing concentrated formic acid to drop into concentrated sulphuric acid heated by a water-bath. The gas was dried by passage through sulphuric acid and then over soda lime and solid caustic soda.

1236. The carbonyl reaction is extraordinarily sensitive to the presence of air. Simply pouring the hardened fat and catalyst from one vessel to another, suffices to nullify the reaction. Accordingly, after hardening, the fat and catalyst are cooled to 90° to 100° C. in a weak current of hydrogen. Then the vessel is placed in a water-bath at 90° to 92° C. and the hydrogen replaced by carbon monoxide. The gases leaving the reaction flask are passed through a hard glass tube which is heated at one point. Nickel carbonyl is decomposed and forms a mirror on the glass walls in the heated zone. To obtain good adherence of nickel the tube must be thoroughly clean. The separation of nickel is not quantitative. Some carbonyl escapes decomposition in the heating zone, as may be shown by igniting the issuing gas. The flame is colored yellow or if the amount of carbonyl is extremely minute the color is a pale blue. Only a few minutes suffice to secure a heavy nickel mirror.

NICKEL CARBONYL REACTION ON CATALYZERS

Oil	Catalyst	Melting-point of the Hardened Fat	Nickel Mirror
Cotton oil	5 per cent basic nickel formate	50.8	marked
Cotton oil	5 per cent basic nickel formate	51.2	marked
Cotton oil	1 per cent nickel carbonate	49.8	marked
Cotton oil	$\frac{1}{2}$ per cent oxide (Erdmann)	46.2	marked
Pure linseed oil	$\frac{1}{2}$ per cent oxide (Erdmann)	42.4	marked
Whale oil	$\frac{1}{2}$ per cent oxide (Erdmann)	46.8	marked
Linseed oil	$\frac{1}{2}$ per cent oxide (Kahlbaum)	42.5	marked
Linseed oil	$\frac{1}{2}$ per cent oxide (Merck)	40.6	marked
Linseed oil	$\frac{1}{2}$ per cent oxide from nitrate	40.6	marked
Linseed oil	$\frac{1}{2}$ per cent oxide (Kahlbaum)	40.2	marked

1237. If hydrogenation is allowed to progress to a lesser degree, the mirror appears with the carbonyl test. For example, olive oil was hardened to a melting-point of only 17° C. and a positive test for nickel was obtained. If fat hardening is carried out at a temperature below that prescribed by Erdmann, or not over 230° C., blackening of the green nickel oxide does not occur, the color changing only to a grayish green. The iodine number of olive oil, after three and one-half hours hydrogenation under these conditions, fell but one or two units. The carbonyl test was positive, although very weak. A blank test with the same nickel oxide in fresh oil and without treatment with hydrogen, maintained at 90° C., while carbon monoxide was passed through, showed that nickel oxide was not reduced by the monoxide under these conditions.

1238. Since Erdmann has suggested that the reduction of nickel oxide may be brought about by aldehydes contained in the oil, Normann and Pungs tested the reducing effect of formaldehyde and benzaldehyde, two of the most powerful reducing aldehydes. They heated a mixture of edible oil, aldehyde and nickel oxide on an oil-bath at 225° C., without introducing hydrogen. No reduction of the oxide was noted; in one case, olive oil, benzaldehyde and green nickel oxide were heated to about 250° for four hours, using a reflux condenser; but no blackening of the oxide was perceptible. The likelihood of reduction by the aldehydes of fatty oils, therefore, appears to be remote.

1239. In the table below the results of the carbonyl reaction at a temperature of 50° C. are given when employing olive oil of iodine No. 82, freed from aldehydes by the silver nitrate method of Becchi, and hydrogenating at a temperature of 250° C. in the first four tests and at 230° C. in the remaining tests. Thus at 50° C. as well as at 90° C., the carbonyl reaction is obtained from catalyst in oil. Even at 30° C. the carbonyl is slowly formed. At 30° C. the necessary contact of the monoxide with the relatively thick oil is difficult to bring about.

1240. An endeavor was made to make the carbonyl test a quantitative one. To this end, the glass tube in which the nickel carbonyl was decomposed, was filled with fragments of porcelain and was heated in two or more places. It was then noted whether or not at the place of heating most remote from the point of entry of the carbonyl, any nickel was deposited. The exit gases were ignited and the color of the flame noted. It should be a pure blue. From 1 g. of catalyst held at a temperature of 90° C. for four hours 0.05 g. of nickel was obtained. A second test conducted for four days gave 0.07 g. nickel. Even then the reaction had not been completed. Nickel carbonyl was still being formed in the oil.

NICKEL CARBONYL FORMATION AT 50° C.

Catalyst	Melting-point of the Hardened Fat	Iodine Number	Carbonyl Test
1 per cent nickel oxide (ic) Kahlbaum....	15.5	68.4	Heavy nickel mirror
1 per cent nickel oxide (ic) Kahlbaum....	49.6	37.1	Heavy nickel mirror
1 per cent nickel oxide (ous)	27.0	67.4	Heavy nickel mirror
1 per cent nickel oxide (ous)	49.8	38.0	Heavy nickel mirror
1 per cent nickel oxide (ous) Temp. 230° ..	Liquid	78.0	Distinct mirror
1 per cent nickel oxide (ous) Temp. 230° ..	Liquid	79.0	Weak but distinct mirror

1241. If the residue of nickel in the oil is regarded as negligible, Normann and Pungs assume the hardening to have been carried out with a catalyst consisting of about 7 per cent of metallic nickel on upwards of 90 per cent of nickel oxide serving as a carrier. The question then arose as to the possibility of so small a proportion of nickel effecting the degree of hydrogenation noted. Normann and Pungs regard the question as answered as a result of their practical experience. It is stated that a catalyst of this composition, when carefully and skillfully prepared, gives good results not only in the laboratory but also on the large scale. From repeated use more nickel is likely to be reduced as a result of the continued contact with hydrogen.

1242. A nickel-kieselguhr catalyst was prepared by reduction at 450° to 500° C. at which temperature the existence of a suboxide is regarded as entirely excluded. The content of free nickel, calculated from a determination of the volume of hydrogen evolved by sulphuric

acid was 4.2 per cent. By the addition of only 1 per cent of this catalyst to refined sesame oil, the melting-point was raised to 45° C. on hydrogenating for one hour. Normann and Pungs do not record the amount of nickel computed from the mixing formula of this catalyst so that it does not appear whether or not this calculated proportion checks with the result of the hydrogen evolution determination.

1243. In every instance, the catalyst material, which before hardening, did not contain free metal, after hardening, showed the presence of the metal, hence, irrespective of the question of formation of nickel suboxide or other assumed reduction product between nickel oxide and the metal, it is concluded that fat hardening does not occur in the absence of the free metal and that some substance other than the free metal is an active catalytic agent, as contended by Erdmann, has not been proven.

1244. Normann. *Chem. Ztg.*, **40**, 757; *J.S.C.I.*, 1916, **35**, 1070; same abstract in *Chem. Abst.* 1917, **11**, 1321. As abstracted this article is self-contradictory. The statement is first made that nickel oxides have no activity until reduced to metal. Normann then goes on to compare the activity of the oxide and of the metal in a manner which implies some activity of the oxide catalyst *per se*, an admission nowhere else made by this author. At any rate, he reaffirms the superiority of the metallic catalyst.

1245. Armstrong and Hilditch. *Proc. Roy. Soc.*, 1921, **99A**, 490. A study of the conditions of reduction of nickel catalysts. The superior activity of a partially reduced nickel catalyst is demonstrated.⁴ The explanation is that the oxide residue acts as a carrier, conferring on the catalyst the enhanced activity and robustness characteristic of a supported catalyst, though not to the same degree as this is effected by such a carrier as kieselguhr. Armstrong and Hilditch show experimentally that, in a partially reduced catalyst, the dominant factor of activity is the condition of the surface layer of reduced nickel. Complete reduction of an unsupported nickel catalyst is accompanied by considerable shrinkage: no appreciable diminution of bulk occurs when nickel oxide spread on kieselguhr is completely reduced to metal. Correspondingly, an unsupported nickel catalyst reaches its maximum activity before complete reduction and if the reduction is pushed further a decline in activity occurs. But with a nickel catalyst supported on kieselguhr this fall of activity on complete reduction is not observed. It is, therefore, evident that the enhanced activity of a partially reduced unsupported nickel catalyst requires for its explanation no lower oxides of nickel, but is amply explained by the condition of the metal on the surface of the contact mass.⁵

1246. Maxted. *Chem. Age* (London), 1922, **6**, 542. No active oxide of nickel has been prepared without the use of such conditions that partial reduction to metal was also possible.

1247. Kahlenburg and Ritter. *J. Phys. Chem.*, 1921, **25**, 89. Nickel chloride reduced with hydrogen at 180–250° C. is a good catalyst for hydrogenation of oils. Such a catalyst contains no oxide.

1248. Kelber, *Ber.*, 1924, **57**, 136, 142. Catalyst made by reduction of nickel cyanide with hydrogen differed in no respect from a catalyst reduced from an oxygenated compound.

1249. Non-existence of Nickel Suboxide. Levi and Tacchini⁶ conclude from an examination of five nickel preparations, which should have contained the suboxide if it existed, that no known method of preparation yields a suboxide of nickel. The method for irregularly oriented crystal powders and X-rays arising from an anticathode of copper were used. Five preparations of nickel were examined: (1) finely divided nickel obtained by reduction of nickel monoxide in a stream of hydrogen; (2) a reduction product of nickeloso-nickelic oxide (Ni_3O_4) containing 87.34 per cent of nickel (i.e., Ni_2O by calculation)⁷; (3) nickel reduced at 1000° C. and then placed in cold oxygen, which gave a product containing 85.2 per cent nickel ($\text{Ni}_{1.57}\text{O}$); (4) a product obtained by further reduction of the material mentioned

⁴ U. S. Pat. 1,159,480, Nov. 9, 1915, to Ellis, describes what is termed a semi-reduced hydrogenation catalyst the preparation of which is carried out by the careful reduction of nickel oxide or hydrate to effect only partial reduction, ordinarily about one-half of the oxygen being removed, affording an intimate mixture of catalytic nickel combined with nickel oxide or certain of the suboxides. Besides hydrogen, other reducing gases or vapors, namely, water gas, carbon monoxide and the vapor of alcohol, are mentioned. A catalytically active nickel black is produced by Boyce by reducing nickel oxide with hydrogen. The action is stopped before complete reduction takes place, leaving a product which is predominately black. (Canad. Pat. 171,436, 1916; *Chem. Abst.*, **1918**, 749).

⁵ Rideal and Taylor, *loc. cit.*, 2nd edition, p. 268.

⁶ *Gazz. chim. ital.*, 1925, **55**, 28.

⁷ Glaser, *Z. anorg. Chem.*, 1903, **36**, 19.

under (2) and which contained 80.06 per cent nickel; (5) pure nickel monoxide. The results show that (2), (3) and (4) are mixtures of nickel and nickel monoxide. Readings, diagrams and photographs are given.

1250. From a study of the rates of reduction of nickel monoxide prepared in various ways, Berger,⁸ also, had concluded that there was no suboxide of nickel.

⁸ *Compt. rend.*, 1922, **174**, 1341; *Chem. Abst.*, 1922, **16**, 2457. In an earlier research, *Compt. Rend.*, **158**, 668, Berger found, as he then believed, some indication of the existence of Ni_2O .

CHAPTER XIII

NON-NICKEL BASE METAL—NON-METAL CATALYSTS AND CARBONYLS

BASE METAL—NON-NICKEL CATALYSTS

1300. The base metals other than nickel and cobalt have been but little used as single hydrogenation catalysts, except in a tentative way. As co-catalysts they have more vogue, as is seen in Chapter VI on Promoters. Recently non-nickel base metals, and especially their oxides, have come into notice as catalysts in the carbon oxide reduction synthesis (methanol, synthol, synthin, etc.), in the liquefaction of coal and in hydrogenation—cracking of mineral oils. This development is not treated here, but under the syntheses in question.

1301. Much of what has been written under nickel catalysts is either expressly or implicitly applicable, *mutatis mutandis*, to the preparation of catalysts from other base metals.

1302. Comparison of Catalytic Activity and of Adsorptive Power of Various Metals. Pease and Stewart¹ impregnated diatomite brick with solutions of the nitrates of iron, of cobalt, of nickel, of copper and of silver, the proportions in each case being 1 g. atom metal to 100 g. brick. The effect of each of these catalysts on the hydrogenation of ethylene and its adsorptive power for the reactants was measured. Cobalt and nickel caused instant hydrogenation of ethylene at -20°C. ; iron was moderately active at 0°C. , copper at 50°C. , silver at 100°C. Hydrogen was more largely absorbed by nickel and cobalt than by the other metals: iron was the best adsorbent for ethylene. The rate of hydrogenation was shown to depend on the hydrogen concentration.

1303. Müller² finds that catalytic activity of iron and nickel, especially in connection with processes for the introduction of hydrogen into glycerides of unsaturated fatty acids, is considerably augmented and caused to resemble in activity the catalytic properties of the noble metals, such as palladium, if the former metals after ignition in hydrogen are heated in a stream of carbonic acid gas in order, apparently, to destroy the metal hydrides which are formed and convert the catalyzer into the pure metal. Müller says the process also makes possible the elimination of finely divided catalyzer, whose production and application the patentee states is accompanied with many difficulties, and its replacement by coarse fragments of metal, such as filings and shavings of iron, nickel

¹ *J. Am. Chem. Soc.*, 1927, **49**, 2783; *Chem. Abst.*, 1928, **22**, 345.

² *Seifen. Ztg.* (1913), 747; French Pat. 540,703 (1912); Brit. Pat. 22,092, Sept. 28, 1912, to Müller, Speisefettfabr. A.-G.

and copper, first igniting the latter in hydrogen and then in carbonic acid gas. He states that common iron filings caused a reduction of the iodine number of only 2½ per cent in two hours, while using filings which had been treated with carbon dioxide the iodine number was reduced 25 per cent.

1304. Copper Catalysts (for Methanol Synthesis). Audibert and Raineau³ made copper catalysts in various ways and compared their activities. Although these tests related only to the methanol synthesis, i.e., to the reduction of carbon monoxide by hydrogen at high pressure (150 atm.), it is likely that the results are of more general application.

1305. Hydrated cupric oxide. The black precipitate formed when a solution of an alkaline hydroxide is added to a boiling aqueous solution of copper nitrate is commonly called tetra-cupric hydrate $(\text{CuO})_4 \cdot \text{H}_2\text{O}$. This, reduced with hydrogen, gave Sabatier a copper of low density, purple color and high catalytic activity. If the hydrate is dehydrated below 300° C. the anhydrous oxide obtained is of the same appearance and bulk and commences to undergo reduction at the same temperature as the hydrate. Dehydration at higher temperature gave a product of different color and apparent density. Four catalysts were made and compared. These had been reduced from thoroughly washed hydrate dehydrated at different temperatures for three to four hours. Other conditions being equal it was found that the catalysts made from material dried at 200° C. and at 270° C. showed 30 per cent more activity than two other catalysts made, one from material dried at 100° C., the other from material dried at 700° C. From this Audibert and Raineau draw the credible but not altogether obvious conclusion of "the necessity of employing low-temperature dehydration of the cupric hydrate." On the basis of the experiment cited it would have been safer to say, merely, that drying at 100° C. and at 700° C. both gave poor catalysts, while drying at 200° C. and at 270° C. gave active catalysts.

1306. Fused Cupric Oxide. This, on reduction, gave a poor catalyst.

1307. Cupric Oxide from Ignition of Organic Salts. Oxides made by low-temperature decomposition of the acetate and the formate, gave catalysts of the same activity as those reduced from the hydrate.

1308. Cuprous Oxide. On reduction cuprous oxide yielded catalysts of the same order of activity as those made from cupric hydrate.

1309. Cupric Oxide Precipitated from Chloride or Sulphate. The catalysts prepared from these were inactive, a result attributed by Audibert and Raineau to poisoning by adsorbed anion.

1310. Cupric Oxide Obtained by Precipitating Nitrate Solution in the Cold. The oxide precipitated in this way by ammonia on reduction yielded copper devoid of catalytic activity. That this was not due to absence of traces of fixed alkali in the other, active, catalysts, was shown conclusively by washing the latter and by adding fixed alkali to the ammonia precipitate.

1311. The relation between the activity of a copper catalyst in the methanol decomposition⁴ and the temperature at which the hydroxide was precipitated

³ *Ind. Eng. Chem.*, 1928, **20**, 1105.

⁴ See para. 5354.

has been examined by Frolich, Fenske and Quiggle.⁵ They found that the catalytic activity of copper catalysts prepared by reduction at 200° of the hydroxide obtained on precipitating copper nitrate solution with ammonia varied with the temperature of precipitation. A maximum activity was obtained when the hydroxide was precipitated at 22°. X-ray examination indicates that small particle size of the dry hydroxide gel is associated with the more active catalysts. A minimum particle size at 22° may be produced as the result of two opposing factors, viz., the tendency for the initial particle size to decrease with falling temperature of precipitation, and the tendency for the initially formed particles to grow while the hydroxide is drying at 110°.

1312. Attempts to Activate Copper for Catalytic Hydrogenation by Oxidation and Reduction.⁶ A copper catalyst of low porosity and high activity prepared by low-temperature oxidation and reduction of well-sintered copper was only temporarily active in the hydrogenation of ethylene. This deactivation was uninfluenced by the temperature of oxidation or reduction of the copper and by the temperature of evacuation of the catalyst bulb. Neither was it due to the fixation of surface crystals on the catalyst. Apparently an atomic reaction occurs on the metal surface as a result of catalytic action, whereby the atoms become momentarily labile and may subsequently become oriented to a crystal.⁷

1313. Alkaline Copper Oxide Catalyst for Ester Reduction. Bouvier and Blanc use a catalyst composed of partially reduced copper oxide and hydroxide to which alkali is added for the reduction of alkyl esters and, in particular, of methyl formate with hydrogen at 80° to 160° C. Care must be taken not to carry the reduction of the catalyst to the formation of metallic copper. Methyl formate thus treated yields methanol.⁸

1314. Preparation of Metals in Active Form by Precipitation with Chromous Salts. From a solution of copper sulphate a chromous salt throws down a precipitate which has been thought to be cuprous oxide. This substance is endowed with marked catalytic activity. Piccard and Thomas⁹ find that it is not the oxide, though it is readily oxidizable. It contains 98.9 per cent of copper. An active silver catalyst is made by reducing a solution of silver perchlorate with chromous acetate in perchloric acid. It forms a white powder containing 99.6 per cent silver and it is twice as active as silver obtained by the action of zinc on silver chloride.

1315. Mixed Zinc and Copper Oxides: Reduction to Zinc. The mixed catalyst, composed, initially, of cupric oxide and zinc oxide, has recently acquired importance in connection with carbon monoxide syntheses. It is, therefore, interesting to learn from Rogers¹⁰ that zinc oxide, mixed with copper oxide, can be reduced completely to metal by hydrogen at 300° C. The point of this observation is that hitherto the zinc oxide has been classed among the refractory oxide catalysts.

⁵ *J. Am. Chem. Soc.*, 1929, **51**, 61; *Brit. Chem. Abst.*, **1929**, 274A.

⁶ Pease and Griffin, *Am. Chem. Soc.*, 1927, **49**, 25.

⁷ *Brit. Chem. Abst.*, **1927**, 215A.

⁸ U. S. Pat. 1,605,093, Nov. 2, 1926.

⁹ *Helv. Chim. Acta*, 1923, **6**, 1044; *J.S.C.I.*, 1924, 99B.

¹⁰ *J. Am. Chem. Soc.*, 1927, **49**, 1432.

1316. Iron Oxide: Catalytic Activity; Preparation of Catalyst. Senderens states that iron prepared from ferric oxide is only of low efficiency, its activity being lower than that of the other metals. Marwedel,¹¹ however, has found oxides of iron to be effective as catalyzers in the reduction of nitro-bodies. The process according to Marwedel consists in mixing the nitro-bodies, in the gaseous state, with reducing gases, and passing the mixtures over heated finely divided ferrous oxide or ferro-ferric oxide. It is advisable to distribute the oxide on inert substances such as asbestos or kieselguhr.

1317. Marwedel points out that in the reduction process described below the iron-oxide compounds remain unchanged, for the reduction of iron oxide compounds to metallic iron by means of hydrogen does not take place until the temperature exceeds 400° C.

1318. The following example describes the process as used for reducing nitrobenzene to aniline; but it is stated that other nitro-bodies, such as nitro-toluol or nitroxylol, can also be reduced in the same way.

1319. Example: An iron pipe is charged with asbestos. Ferrous oxide, or ferro-ferric oxide, is distributed on the surface of the asbestos. The vapors of the nitrobenzene and hydrogen, or water-gas are introduced. The nitrobenzene and hydrogen mixture passes over the oxide. The pipe is heated, the temperature being kept above the boiling temperature of nitrobenzene and below the temperature at which a reduction of the iron oxide compounds takes place. The relative proportions of the mixture of nitrobenzene and hydrogen are such that about 70 parts by weight of hydrogen are employed to 1000 parts, by weight, of nitrobenzene. The gaseous mixture issues from the apparatus and is passed through a condensing coil, and is collected in a receiver, connected to a vacuum pump. Care must be taken to keep a sufficient quantity of hydrogen present to prevent the reduction of the nitrobenzene from being arrested at intermediate stages (azobenzol or hydrazobenzol). In order to prevent incomplete reduction an excess of hydrogen is used; which excess can be collected and again passed through the reducing chamber.

1320. Tin as a Hydrogenation Catalyst. Brown and Henke¹² prepared tin catalysts by reduction of stannous hydroxide directly and of stannic oxide made by oxidation of stannous hydroxide: the latter proved the better catalyst. Rather coarse lumps worked better than a powder. The reductions carried out were: nitrobenzene to aniline (99 per cent yield); ortho-nitrotoluene to ortho-toluidine (94 to 99 per cent); ortho-nitroanisole to ortho-anisidine (93 per cent). Tin catalysts allow more latitude in operating temperature than do most catalysts: the best range of temperature in a glass tube seems to be 275° to 294° C. A higher temperature is necessary in glass than in iron tubes.¹³

1321. Lead: Catalytic Activity. Madenwald, Henke and Brown¹⁴ have measured the activity of various lead catalysts in the reduction of nitrobenzene

¹¹ U. S. Pat. 1,124,776, Jan. 12, 1915.

¹² *J. Phys. Chem.*, 1923, **27**, 739; *Chem. Abst.*, 1924, **18**, 1936.

¹³ Molten tin and tin in other forms are used in oil cracking and allied processes.

¹⁴ *J. Phys. Chem.*, 1927, **31**, 862.

by hydrogen. Light red lead, heavy red lead, and a light and a heavy litharge, prepared from recrystallized lead nitrate by varying heat treatments, on reduction by hydrogen at 308° gave the catalysts used. The activity of the catalysts increased with use, but more slowly than is the case with copper catalysts. It also increased more rapidly in an iron than in a glass tube. The initial activity of the different samples varies, but the final activity is the same. The optimum temperature for the reduction of nitrobenzene is 308°, and one catalyst prepared from heavy litharge maintained a 97 per cent yield of aniline for approximately 200 experiments. Grinding the catalyst had no permanent effect on its activity. Treatment with hydrogen alone destroyed the activity. The optimum rate of flow is 14 liters of hydrogen and 4 g. of nitrobenzene per hour at 308°. Appreciable yields of azobenzene (up to 25 per cent) were obtained only during the first few runs.¹⁵

RELEVANT REFERENCES

1322. Jaeger. U. S. Pat. 1,694,620, Dec. 11, 1928; Brit. Pat. 286,212, Feb. 28, 1927; 279,466, Oct. 19, 1927; 304,640; 306,803 (convention date Feb. 25, 1928); *Chem. Age* (London), 1929, 20, 454. Base exchange compounds of use as catalysts. The description given by Jaeger is voluminous and one of the originals should be consulted for details. Among the uses relevant to our subject are the removal of catalyst poisons, the methanol synthesis, and hydrogenations in general. Jaeger's type of catalyst is exemplified by the following:

Base-exchange materials for use as catalysts are prepared by treating a solution of an alkali silicate with the salt of a metal capable of becoming part of the non-exchangeable nucleus, then with a salt of a metal acid, e.g., vanadic, molybdic, tungstic acid, etc. The gelatinous mass is stirred, filtered, and dried; it may then be subjected to a base-exchange process or heated in a suitable oxidizing or reducing atmosphere to induce the desired catalytic properties. If desired, the zeolite may be incorporated with inert porous material either during or after formation. *Brit. Chem. Abst.*, 1928, 603B.

1323. Komatsu. New functions of reduced copper. *Sezagint, Y. Osaka, Chem. Inst. Dept. Sci. Kyoto Imp. Univ.*, 1927, 203. Copper is characteristically a dehydrogenating and a dehydrating catalyst. Komatsu recognizes three types of copper catalyst: dehydrogenating (from sulphate with excess alkali); dehydrating (from basic copper salt); combined action catalyst (from ignited nitrate).

1324. Komatsu and Kurata. Catalytic activity of reduced copper. *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1925, 8A, 35; a comparative study of the oxidizing and dehydrating catalytic activity of copper, prepared in different ways.

1325. Pease and Harris. Catalytic combination of ethylene and hydrogen in presence of metallic copper. *J. Am. Chem. Soc.*, 1927, 49, 2503; *Chem. Abst.*, 1928, 22, 13. Within the range examined the rate of hydrogenation was proportional to hydrogen concentration. There is a summary and discussion of the results of the series of which this article is the fourth.

NON-METAL CATALYSTS

1326. As primary or sole catalysts non-metals play an insignificant rôle in hydrogenation.

1327. Boron may be used as a catalyzer according to Hildesheimer.¹⁶ If the substrate is a gas it is simply mixed with hydrogen and passed over the boron material; if liquid, it is mixed with boron and hydrogen is passed through it. When the addition of hydrogen is completed the boron is separated by filtration and is ready for use again. The catalytic action is assumed to depend upon the

¹⁵ *Brit. Chem. Abst.*, 1927, 737A.

¹⁶ *Zeitsch. f. angew. Chem.* (1913), Ref. 583.

intermediate formation of boron hydride BH_3 . The rate of conversion is influenced by the temperature and pressure as well as the amount of boron. Cottonseed oil and other unsaturated compounds, such, for example, as ethylene, add hydrogen under these conditions. In place of boron some of its compounds, such as boron hydride, and metallic compounds of boron, such as aluminum boride, may be used. Gases containing hydrogen may be used in place of pure hydrogen.

1328. According to Gordan Hay¹⁷ fine colloidal clay possesses catalytic properties for hydrogenations and oxidations, e.g., in hydrogenation of oils and in oxidation of alcohol to aldehydes. Its activity, is, however, much less than that of the catalysts usually employed, but as a catalyst support it offers great advantages.

REFERENCES

- 1329.** Ruff. Activated charcoals and their adsorptive power. *Z. angew. Chem.*, 1925, **38**, 1164; *Chem. Abst.*, 1926, **20**, 855.
1330. Henglein and Grzenkowsky. Adsorption of gases by wood charcoal at pressures above one atmosphere. *Z. angew. Chem.*, 1925, 1186; *Chem. Abst.*, 1925, **20**, 856.

CARBONYLS

1331. Nickel Catalyst from Nickel Carbonyl. The facts that nickel carbonyl is soluble in fatty oils and that it can be readily decomposed by heating, liberating pure nickel in extremely fine division, were enough to suggest this as a method for preparing a hydrogenation catalyst. Accordingly, a number of patents, dealing with the application of these phenomena, have been taken out, the earliest by Shukoff (Germ. Pat. 241,823, 1910).

1332. Thomas¹⁸ has compared the activity of catalyst prepared by thermal decomposition of nickel carbonyl in the presence of the substrate (cottonseed oil) with that of catalysts made in other ways.

As carbon monoxide is a poison to nickel in hydrogenation in a closed system, care was taken before the test was carried out to remove all traces of the gas by passing hydrogen through the oil at ordinary temperatures for a long period. The activity of this catalyst (*d*) was tested with cottonseed oil, the concentration of nickel being 0.15 per cent. It compared with a catalyst on kieselguhr prepared by reduction with hydrogen (*a*) as follows:

Time (mins.)	Hydrogen absorption (cc.)	
	(a)	(d)
2	58	45
5	149	98
10	149	134
15	339	...
20	385	167

¹⁷ *Chem. Agr.*, 1920, **2**, 194; *Chem. Abst.*, 1920, 1070.

¹⁸ *Loc. cit.*, p. 5.

The activity of nickel prepared by decomposition of the carbonyl is little more than one-fourth that of nickel on kieselguhr prepared by method (a), although it compares favorably with unsupported nickel prepared by reduction. The activity of the latter is slightly lower, but of the same order as (d) above, an absorption of 149 cc. being observed in twenty minutes.

1333. Shukoff claims the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl. On heating to a temperature of 200° or so, the carbonyl is decomposed, setting free, in a nascent state metallic nickel which acts as a catalyzer. Shukoff makes use of this reaction of nickel carbonyl by a method of apparent simplicity. Carbon monoxide is passed into a tube containing finely divided nickel and the nickel carbonyl formed is conducted to the oil, which is heated to about 180°. After sufficient nickel catalyzer has formed in the oil, the carbon monoxide stream is cut off, the temperature raised to 220° or 240° C. and hydrogen gas introduced to bring about hydrogenation.

As an example: Into 8 kilos of cottonseed oil warmed to 180° C. a slow stream of 400 liters of carbon monoxide is passed, which carbon monoxide has previously passed over a long layer of metallic nickel warmed to about 60° C.; finely divided active nickel separates in the oil; the stream of carbon monoxide is then interrupted, the temperature raised to 230° to 240° C., and hydrogen as a slow stream is run into the mixture during a period of five to six hours in an amount of 3000 liters. The reaction mixture on cooling is completely hard; by filtration the nickel can be removed and the product eventually converted into stearic acid.

1334. In the author's laboratory nickel carbonyl has been extensively examined as a source of nickel catalyzer. The carbonyl readily decomposes at temperatures between 125°

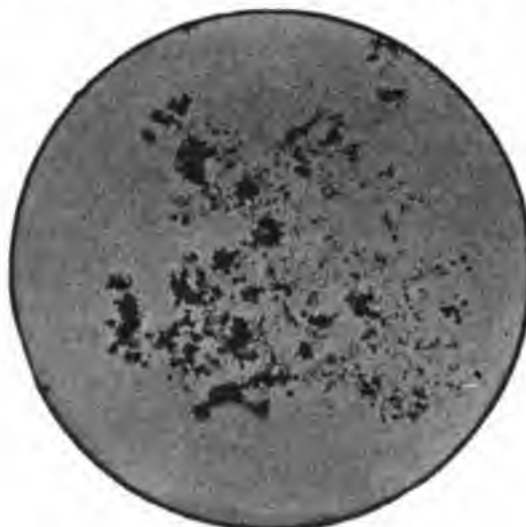


FIG. 23.

Photo-micrograph of Nickel Catalyzer derived from Nickel Carbonyl. $\times 100$.

and 180° C. and when decomposed in the presence of oil under some conditions the resulting nickel is very finely divided and imparts to the oil an inky black color. After standing for days or even weeks the nickel remains in suspension. A sample of cottonseed oil carrying about one-half of one per cent of nickel precipitated from nickel carbonyl was exposed to the action of a current of hydrogen gas under practically atmospheric pressure for a period of one hour and a solid product resulted having a melting-point of 47.6° C. and a refractive index of 1.4445.

1335. The greatest difficulty in the use of nickel carbonyl appears to be the removal of finer portions of the nickel precipitate from the oil after hydrogenation, but this may be accomplished by the observance of due precaution in filtration. The used catalyzer recovered by filtration is still active and may be used until its catalytic properties are spent. The spent material may be regenerated more easily than is the case with catalyzers consisting of nickel supported on a voluminous carrier of inert material.¹⁹

1336. Another modification of the nickel carbonyl process is described by the author²⁰ and involves mixing the requisite amount of nickel carbonyl with hydrogen-gas, or water-gas, or other gas suitable for the purpose and then passing this mixture into the oil to be treated.

The oil is brought to the decomposition temperature of the nickel carbonyl under these circumstances and the metallic nickel catalyzer is liberated in intimate contact with the hydrogen gas, effecting a rapid hydrogenation of the oil.

1337. The employment of nickel carbonyl by Shukoff has been described in the foregoing. In a somewhat similar manner Lessing²¹ makes use of a mixture of hydrogen and a gaseous metallic compound brought into contact with the substance under suitable conditions of temperature and pressure. Lessing states he has found that a great number of substances may be hydrogenated by treating them at elevated temperatures with hydrogen to which a metallic carbonyl vapor, or gas containing a metallic carbonyl, has previously been added; or with a mixture of gases, containing hydrogen in which metal carbonyl has been formed by combination of carbon monoxide, originally in the mixture, with a metal. The rapidity with which the hydrogenation proceeds under these conditions may be explained as the effect of the liberation of elementary metal, the properties of which *in statu nascendi* are known to be very different from those of metal which is merely finely subdivided. Lessing observes that it has already been proposed to use as the catalyzer finely subdivided nickel, made by decomposing nickel carbonyl in the heated material prior to the introduction of the hydrogenating gas, but it was not known that technical advantages accrue from conveying the nickel carbonyl into the material simultaneously with the hydrogenating agent so that elementary liberation of nickel occurs in close contact with hydrogen and the substance to be hydrogenated. These advantages are that the proportion of catalyzer is very much reduced and the reaction proceeds much more rapidly. Lessing carries out his process in various ways. It is convenient to introduce nickel carbonyl into the hydrogen gas by passing a mixture of the latter with carbon monoxide over reduced nickel in the well-known manner for making nickel carbonyl.

1338. The mixture of gases employed need not be of great purity and may be made from water-gas, or by the thermal decomposition of coal gas or of coke-oven gas or of hydrocarbons of any kind, but best results are obtained when the amount of carbon monoxide in the gases is limited to that requisite for forming the nickel carbonyl necessary for the reaction, and in any case the proportion of carbon monoxide in the mixture should not exceed 25 per cent. For example, when an oil such as a glyceride or a fatty acid is being hydrogenated, the simplest mode of operating consists in passing hydrogen containing 5 to 10 per cent of carbon monoxide first through a volatilizer charged with reduced nickel and then through the oil contained in a closed vessel heated to a suitable temperature, say from 200° to 240° C. The gases passing away from the vessel are returned to the volatilizer to be used again, hydrogen or a gas rich therein being added to compensate for that absorbed by the oil. The proportion of nickel required for the hydrogenation is very small; under proper conditions excellent results can be obtained with a proportion equivalent to 0.1 part of nickel to 100 parts of oil.

1339. Crossley²² refers to British patent to Lessing, 18,998, of 1912, and states that the process described therein appears to differ materially from others, more particularly in the novel method for bringing catalyst and oil in contact. According to this process hydrogen containing 5 to 10 per cent of carbon monoxide, such as may easily be prepared from water-gas or the thermal decomposition of coal gas or hydrocarbons, is passed over reduced nickel, with formation of nickel carbonyl. The nickel need not be pure, but in the form of such complex mixtures as are obtained in the treatment and reduction of nickel ores. The mixture of hydrogen and any desired proportion of nickel carbonyl is then passed into the substance to

¹⁹ Apparatus adapted for handling nickel carbonyl and hydrogenating oils with the nickel material obtained by its decomposition is shown in U. S. Pat. to Ellis, 1,095,144, Apr. 28, 1914.

²⁰ U. S. Pat. 1,154,495, Sept. 21, 1915.

²¹ Brit. Pat. 18,998, 1912.

²² *Pharm. Soc.*, Apr. 21, 1914; *Pharm. J.*, 1914, 92, 604, 637 and 676; *J.S.C.I.*, 1914, 1135.

be hydrogenated at a temperature between 200° to 240° C. when the nickel carbonyl is decomposed and elementary nickel, in a very pure and particularly active form, is produced. Fresh nickel carbonyl is always passing into the substance to be hydrogenated, and the nickel is believed to act in the nascent condition at the moment of decomposition of the nickel carbonyl. This, he states, seems to be borne out by the fact that if the same percentage of nickel be introduced into an oil as nickel carbonyl, the latter decomposed and then hydrogen passed in, there is practically no result from the commercial point of view.

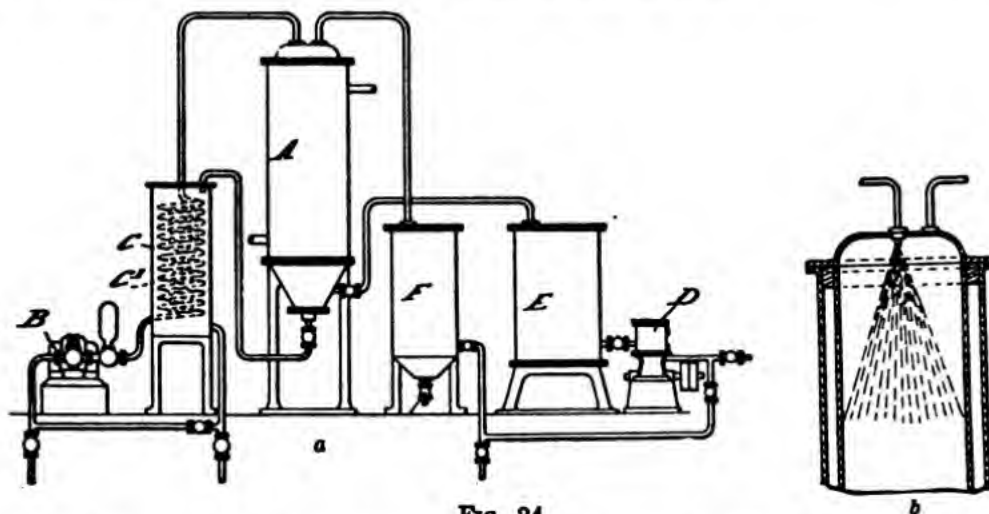


FIG. 24.

Figure 24a is a view of a hydrogenating apparatus suggested by Lessing and Fig. 24b represents a section of the upper portion of the hydrogenating vessel showing a spraying nozzle through which the liquid to be treated may be forced. A is the vessel in which hydrogenation occurs. The substance to be hydrogenated is pumped from a supply tank through a pre-heater contained in a tank C, into vessel A which is heated by a steam jacket. The hydrogenated substance is forced by the pressure from vessel A into the tank C where it is used as heating agent. If finished it is run off; if not finished, it is returned by the circuit shown. The gases enter on the right, are compressed by compressor D, and forced through the volatilizier E, passing therein over reduced nickel. The gases issuing from volatilizier E and containing nickel carbonyl then enter vessel A. The gases left unabsorbed and now free from nickel issue from the vessel A through the right-hand outlet at the top of A and are passed through cooler F and can be either discharged or returned into circulation. Any oil carried along with the gases is deposited in the cooler F and may be run off.

1340. The development of the oil-hardening industry has been in the direction of simplification. For this reason nickel carbonyl has failed to retain an important place as a source of catalyst for the hydrogenation of oils. Nevertheless interest in the carbonyls in general is considerable. There are three reasons for this. In two youthful but lusty twin industrial developments of hydrogenation—the liquefaction of coal and the carbon oxide syntheses—the carbonyls figure as a source of trouble, as a source of catalyst and as an eliminator of trouble. We shall see that in certain of these processes it is deemed necessary to avoid contact between the reactant gases and any metal capable, in the prevailing conditions, of forming carbonyls. Again the carbonyls, undergoing thermal decomposition, deposit metals in a condition of exquisite fineness. This fact has been utilized for the preparation of catalysts. Thirdly, carbonyls, especially iron carbonyls, in light motor fuels, prevent premature explosion (detonation

"knock," "pinking"). For these reasons we are presenting information about these singular metallic compounds.

1340. To prepare nickel carbonyl a combustion tube is filled with nickel oxide and this is reduced by hydrogen at about 400°; after cooling the nickel to about 100°, pure dry carbon monoxide is passed over it without further heating, and the issuing gas is led through a tube placed in a freezing mixture; the major portion of the nickel compound condenses as a colorless liquid.

1341. Nickel carbonyl thus prepared is a colorless liquid, which boils at 43° under 751-mm. pressure: its relative density at 17° is 1.3185. It solidifies at -25° to a mass of needle-shaped crystals. Its composition is represented by the formula $\text{Ni}(\text{CO})_4$. It dissolves in alcohol, and more readily in benzene and chloroform; dilute acids and alkalis have no action on it, but it is oxidized by concentrated nitric acid. It reduces an ammoniacal solution of cupric chloride, and also causes the separation of silver from an ammoniacal solution of silver chloride. It interacts with chlorine, forming nickel chloride and carbon oxychloride. It is decomposed at 180° (in boiling aniline vapor) into nickel and carbon monoxide. The atomic weight of the deposited metal was found in three experiments to be 58.52 to 58.64, a result closely corresponding with Russell's value, 58.74.

1342. The reactions of nickel carbonyl are generally those dependent upon the presence in it of nickel, but when they are induced gently and at low temperature, bodies comparable to organo-metallic compounds are formed. The vapor of nickel is not sensibly soluble in water or dilute acid or alkaline solutions or cuprous chloride. Hydrocarbons are its natural solvents; spirits of turpentine is specially suitable, and can be used for determining it. Explosion of a mixture of nickel carbonyl and oxygen can be effected by violent agitation over mercury as well as by direct ignition. Slow union takes place when such a mixture is kept in contact with a little water. In contact with strong sulphuric acid dry liquid nickel carbonyl explodes after a short interval, but if in the form of vapor and diluted with nitrogen it is decomposed gradually, the theoretical quantity of carbon monoxide being liberated. Strong caustic potash has no perceptible action on nickel carbonyl. Gaseous ammonia does not act immediately *per se*, but if a little oxygen be added, fumes are produced, and if the action of oxygen be continued a whitish deposit of complex composition is gradually formed which is destroyed with charring on being heated.

1343. Sulphuretted hydrogen acts on nickel carbonyl vapor, mixed with nitrogen in the cold, a black sulphide (of nickel) being precipitated. Phosphoretted hydrogen under similar conditions gives a brilliant black deposit. Nitric oxide if mixed with nickel carbonyl vapor, diluted with nitrogen, or passed into the liquid itself, produces blue fumes, which fill the whole vessel. The formation of nickel carbonyl proves carbon monoxide to be capable of forming organo-metallic compounds similar to those derived from hydrocarbons, and analogous to the salts of rhodizonic and croconic acids produced by the union of the condensed derivatives of carbon monoxide with an alkaline metal. Nickel carbonyl serves as an example of the tendency of carbon monoxide to form loose

combinations and products of condensation, in virtue of its character as an unsaturated body.

1344. Nickel carbonyl, according to Berthelot,²³ can be preserved under water, but if contained in a bottle with an ordinary ground-in stopper becomes slowly oxidized, and a layer of apple-green nickel hydrate is formed, which is free from carbon. A portion of it, however, makes its way out of the bottle and is oxidized, forming a fume which is deposited on adjacent objects.

1345. When attacked by oxidizing agents, e.g., nitric acid, chlorine, or bromine or by sulphur, decomposition ensues, nickel salts being formed and carbon dioxide liberated. Metals, alkalis, non-oxidizing acids and the salts of other metals produce no change. Nickel carbonates of composition varying with the hygroscopic state of the atmosphere are formed by exposing the liquid to the action of the air. These precipitates dissolve easily in dilute acid. An intense blue coloration is obtained when nitric oxide is passed through a solution of nickel carbonyl in alcohol (Berthelot).

Nickel carbonyl is very diamagnetic, and an almost perfect non-conductor of electricity (Quincke). All other nickel compounds are paramagnetic. It is opaque for rays beyond the wave length 3820, and its flame gives a continuous spectrum (Liveing and Dewar).

Perkin found the power of magnetic rotation of nickel carbonyl to be greater than that of any other substance he has examined, except phosphorus. Mond and Nasini found the atomic refraction to be about 2.5 times as large as in any other nickel compound, and the former proved it to have great refractive and dispersive powers. The atomic refraction of a liquid ferro-carbonyl bears about the same ratio to the atomic refraction of other iron compounds. This ferro-carbonyl is similar in preparation and properties to the nickel carbonyl, and at 180° C. the iron is thrown down in bright mirror-like form, carbon monoxide being liberated. Its composition is $\text{Fe}(\text{CO})_5$.

1346. To extract nickel from its ores Mond uses an apparatus, Fig. 25, consisting of a cylinder divided into many compartments, through which the prop-

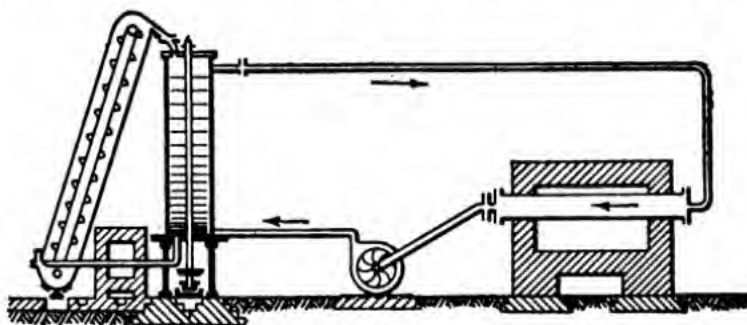


FIG. 25.

erly prepared ore is passed very slowly by means of stirrers attached to a shaft. On leaving the bottom of this cylinder the ore passes through a transporting screw, and from this to an elevator which returns it to the top of the cylinder, so that it passes many times through the cylinder until all the nickel is volatilized. Into the bottom of this cylinder carbonic oxide is passed, which being charged with nickel carbonyl vapor leaves at the top, and passes through the conduits shown into tubes set in a furnace, and heated to 200° C. Here the nickel separates from the nickel carbonyl. The carbonic oxide is regenerated and taken back

²³ *Bull. Soc. Chim.*, 1892, 434.

to the cylinder by means of a fan, so that the same gas is made to carry fresh quantities of nickel out of the ore in the cylinder, and to deposit it in the tubes an infinite number of times. When the carbonic oxide comes out at the top of the cylinder it passes through a filter to catch any dust it may contain. The carbonic oxide, on escaping from the depositing tubes, is passed through another filter, thence through a lime purifier to absorb any carbon dioxide which may have been formed. By means of this apparatus nickel has been extracted from a great number of ores, in times varying, according to the nature of the ores, from a few hours to several days. A well-illustrated account of the manufacture of nickel by the Mond Nickel Co., Ltd., is contained in *J.S.C.I.*, 1927, **46**, 386.

1347. Nickel carbonyl is decomposed²⁴ by passage through a mass of pellets of metallic nickel, heated to about 200° C., causing nickel to be deposited and the pellets to increase in size. The apparatus consists of a vertical cylinder, in which the pellets are placed, with heating spaces formed by an outer casing. A vertical, cooled, perforated tube for the gaseous carbonyl leads from the top down the center of the mass of pellets, nearly to the bottom of the cylinder. To prevent the pellets cohering, they are kept in motion by continuously withdrawing them from the lower end, mechanically screening them with the assistance of worm conveyors, and returning the small ones by an elevator to a feeding hole at the upper end for further treatment with the carbonyl. The pellets which have sufficiently increased in size are passed from the screen and thence through a valved opening into a collecting chamber.

1348. Preparation of Nickel Carbonyl. A convenient laboratory process for the preparation of nickel carbonyl is given by Laird²⁵ and is described here as improved by van Duin.²⁶ Nickelous oxalate is heated at 290°–300° C. in a current of hydrogen. Over the finely divided nickel so obtained, carbon monoxide dry and oxygen-free, is led at 90° C. The carbonyl can be condensed in a tube surrounded by ice and salt. (Laird used liquid air or carbon dioxide snow and acetone.)

1349. In the preparation of nickel-carbonyl by passing carbon monoxide over reduced nickel deposited on pozzuolana the optimum temperature was 45° C. at a pressure of 3 cm. of mercury. Within reasonable limits the yield of carbonyl from a given volume of carbon monoxide was independent of the rate of flow of the gas, provided the velocity was not so great as to prevent adequate condensation of the product. The coefficient of utilization of the metal was 84 per cent, and of the gas 37 per cent.²⁷

1350. Preparation of Iron Tetracarbonyl. In an article on the derivatives and actions of iron pentacarbonyl Freundlich and Cuy²⁸ give as the best method of preparing the tetracarbonyl to heat the pentacarbonyl, in absence of air, with a slight excess of caustic alkali solution. The carbonyl may be extracted with ether.²⁹

²⁴ Mond, Brit. Pat. 1106, Jan. 14, 1898.

²⁵ *Rec. trav. chim.*, 1927, **46**, 177; *Chem. Abst.*, 1927, **21**, 2624.

²⁶ *Rec. trav. chim.*, 1927, **46**, 381; *Chem. Abst.*, **21**, 1927, 2624.

²⁷ Tassilly, K. Penau, and K. Roux. *Bull. Soc. Chim.*, 1921, **29**, 862–864; *J.S.C.I.*, 1921, **40**, 846A.

²⁸ *Ber.*, 1923, **56B**, 2264; cf. Freundlich and Malchow. *Z. anorg. Chem.*, 1924, **141**, 317.

²⁹ A detailed article on the properties of iron carbonyls by Mittasch will be found in *Z. angew. Chem.*, 1928, 827.

1351. Manufacture of Iron Carbonyl.³⁰ In the manufacture of iron carbonyl by passing carbon monoxide over metallic iron at a high pressure, the speed of reaction is increased when the temperature is raised above 140°, and under such conditions the yield of product is considerably increased by reducing the temperature of the gases before releasing the pressure. The temperature of the reaction gases is reduced by utilizing the heat, while the gases are still under high pressure, for preheating the fresh gases introduced into the apparatus.³¹

1352. A letter from Taylor³² states that the Badische Co.³³ pass carbon monoxide (50–100 atmospheres) over iron heated to 180°–200° C. at a rate such that only 2–8 per cent, by volume, of carbonyl is produced. This method of working avoids condensation of carbonyl on the iron.³⁴

1353. Another method for obtaining iron carbonyl consists in heating scrap iron to 600° C., treating it with air and steam to convert it completely to ferric oxide, then reducing it with hydrogen at 450°–500° C. and finally treating it with carbon monoxide.³⁵

1354. Cobalt Carbonyl. Müller and Keunecke³⁶ produce cobalt carbonyl by acting on metallic cobalt with carbon monoxide under a pressure of at least 5 atmospheres, and cooling the reactant gases, before release of the pressure. The pressure is said to be at least 7.4 atmospheres, with a temperature of 50° C., and 200 atmospheres with a temperature of 150°–170° C. The non-condensed carbonyl may be caught by scrubbing or by cooling to 0° C. All connections must be kept above 50° C.

1354A. Increased yields are obtained in the manufacture of cobalt carbonyl from cobalt and carbon monoxide by excluding oxidizing agents during the preparation of the metal and by passing the carbon monoxide over a catalyst of an oxide of manganese or copper or a mixture of these oxides to remove free oxygen.^{36A}

1355. Nickel and Cobalt Carbonyls. A difficulty in the manufacture of these carbonyls is due to the passivity of the metals. Highly reactive metal can be prepared by reducing the hydroxide precipitated from the solutions of the com-

³⁰ Brit. Pat. 250,132, Nov. 25, 1925, to Johnson from the Badische Co.

³¹ Brit. Chem. Abst., 1926, 487B. Details and modifications in operating conditions are given in Brit. Pat. 259,407 to the same patentee; Brit. Pat. 298,714, July 28, 1927, applies the same process to the preparation of cobalt carbonyl (Chem. Abst., 1929, 23, 3058).

³² J.S.C.I., 1929, 222.

³³ Brit. Pat. 244,895, Nov. 26, 1924.

³⁴ Brit. Pat. 269,625, Jan. 11, 1926, prescribes elevated temperatures and (preferably) elevated pressures and carbon monoxide flowing very slowly, if at all. The product is led to cool surfaces outside the reaction zone. (Chem. Abst., 1928, 22, 1446.) These surfaces are very near the reaction zone and the gas reaches them by diffusion or convection (Brit. Chem. Abst., 1927, 481B).

³⁵ Canadian Pat. 284,972, Nov. 20, 1928, to Schlecht and Kennecke (assigned to I. G.); Chem. Abst., 1929, 23, 938. Cf., French Pat. 652,594, Apr. 12, 1928 to the I. G., for a similar method, applied specifically to the preparation of the carbonyls of iron, nickel and cobalt (Chem. Abst., 1929, 23, 3547).

³⁶ Canadian Pat. 278,950, Mar. 27, 1928; Brit. Pat. 298,714, July 28, 1927.

^{36A} Brit. Pat. 307,112, Mar. 12, 1907, to Johnson (from the I. G.); Brit. Chem. Abst., 1929, 393B.

plex ammonium compounds. Precipitation of the metals by zinc may also be used.³⁷

1356. Carbonyl as a Catalyst.³⁸ In the synthin process for producing hydrocarbons from mixtures of hydrogen and carbon monoxide, with substantially less hydrogen than the theoretical quantity for forming methane, a metal prepared from the carbonyl may serve as catalyst.

1357. Pure Iron from the Carbonyl.³⁹ A method is described of preparing pure iron by thermal decomposition of the carbonyl. The essential feature is the decomposition of the carbonyl without bringing it in contact with the hot walls of a reaction vessel. Important points also are methods for controlling the reaction temperature. The original should be consulted for details. The interest to our subject matter is double: first, the iron so produced is used as a catalyst;⁴⁰ second, other catalytic metals are produced in fine powder by the same process.⁴¹

1358. Cobalt, Nickel and Molybdenum.⁴² The process mentioned in the preceding paragraph is applied to the obtaining of cobalt, nickel and molybdenum in a finely divided form. In each case the carbonyl may be dissolved (e.g., in benzene) or it may be sprayed into the free space of the reaction chamber.⁴³

1359. Metallic Colloids and Knock Suppression. Experiments show that nickel sols prepared by heating nickel carbonyl in boiling hexane increase the highest useful compression ratio (H.U.C.R.) of gasoline to nearly the same extent as undecomposed nickel carbonyl, but that by increasing the temperature of decomposition to 85° the improvement becomes negligible. Lead tetraethyl behaves similarly, the lead sol produced at 250° giving an increase in H.U.C.R. of 5 per cent, but that prepared at 300° shows no increase.⁴⁴

1360. Iron Carbonyl in Motor Fuel. The rôle of iron carbonyl as an "anti-knock" constituent of fuel for internal combustion engines is expounded in an article published in 1926 at the behest of the Badische Co.⁴⁵ The iron pentacarbonyl is described as an orange-colored fluid, sp. gr. 1.45. It boils at 300° C. and its flash-point is 20° C. It evaporates about as does gasoline. It is miscible with gasoline in all proportions. It decomposes in light but is otherwise stable. As to the anti-knock potency of the carbonyl, the effect produced by the addition

³⁷ Brit. Pat. application 296,558, Sept. 5, 1927, by Johnson (from the I. G.); French Pat. 650,839, Mar. 14, 1928.

³⁸ U. S. Pat. 1,698,602, Jan. 8, 1929, to Mittasch, Müller, Schlecht and Schubardt, assigned to the I. G.

³⁹ Brit. Pat. 269,677, Jan. 23, 1926 (to Johnson, an I. G. communication).

⁴⁰ E. g., according to the I. G. British patent application 271,452.

⁴¹ *Chem. Age*, London, 1927, 16, 534. Cf. Brit. Pat. 281,963, June 25, 1927, same patentee. *Chem. Abst.*, 1928, 22, 3623.

⁴² Brit. Pat. 284,087, Feb. 4, 1927, to the I. G. Farbenind. A.-G.

⁴³ *Chem. Age*, London, 1928, 182, according to Mond and Wallis (*J. Chem. Soc.*, 1922, 121, 29) molybdenum carbonyl, Mo₄(CO)₁₆, is very difficult to prepare.

⁴⁴ Olin and Jebens, *Ind. Eng. Chem.*, 1929, 21, 43; *Brit. Chem. Abst.*, 1929, 159B.

⁴⁵ *Erdoel and Teer*, April 8, 1926. A translation by Trueadell appeared in *Nat. Petroleum News*, June 2, 1926. Cf. Ostwald, *Petroleum*, 1929, May 8, 3, and Tegner, *Flight*, 1929, Jan. 31; *Mech. Engr.*, 1929, 408.

of 40% of benzene to 60% of gasoline is said to be obtained by using 0.20 to 0.25 of carbonyl.⁴⁶ For iron carbonyl the tetraethyl lead ratio is said by Edgar to be 13 : 5.

1361. Rendering Iron Carbonyl Stable In Light.⁴⁷ This instability in light is avoided by adding to its solution (in gasoline) a coloring substance, an organic acid, an ester or an oxygen containing substance of high molecular weight capable of acting as a protective colloid, or a solid hydrocarbon boiling above 275° C. Examples of suitable substances are: the iron compound of acetylacetone, oil brown dye, wool fat, naphthenic acids, rubber. Iron carbonyl alone is liable to spontaneous ignition. To prevent this it is directed⁴⁸ to add liquid hydrocarbons, or halogenated hydrocarbons or alcohols.⁴⁹

1362. The instability of carbonyls in light is utilized for removing them from organic liquids such as synthetic methane. Such liquids containing less than 10 per cent of carbonyl are exposed to ultra-violet radiation for this purpose.⁵⁰

1363. Fixation of Unsaturated Molecules by Metals Produced from Organo-metallic Derivatives.⁵¹ On keeping a solution of ferrous ethyl iodide, metallic iron is deposited as a mirror, ethylene and ethane also being formed. These changes are explained by the following scheme: $2\text{FeEtI} \rightarrow \text{FeEt}_2 + \text{FeI}_2 \rightarrow 2\text{C}_2\text{H}_4 + \text{FeH}_2 + \text{FeI}_2 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{Fe} + \text{FeI}_2$, where ferrous hydride reduces ethylene to ethane. The iron deposit, which contains traces of ferrous ethyl iodide, is pyrophoric and decomposes water to give hydrogen.

Nickel, cobalt, chromium, and manganese are also produced in active forms from a halide salt and magnesium ethyl bromide, part of the metal being precipitated, the rest remaining in (colloidal) solution. Thus, when an ether-benzene solution of magnesium phenyl bromide is treated, in absence of air, with nickelous chloride, a solution is obtained which (1) rapidly absorbs carbon monoxide, in amount corresponding with the formation of nickel carbonyl; (2) slowly absorbs, per atom of nickel, 2 mols. of nitric oxide (giving a bluish-green solution); (3) absorbs ethylene (2 mols. for each atom of nickel) to give a reddish-brown solution; (4) absorbs acetylene ($\text{Ni} : 3\text{C}_2\text{H}_2$); and (5) rapidly absorbs hydrogen ($2\text{H}_2 : \text{Ni}$), nickel hydride being precipitated as a black, very reactive powder.⁵²

1364. A description of the metallic carbonyls, their technical production, industrial applications and other uses will be found in an article by Mond in *Chimie et Industrie*, 1929, pp. 681-700.

1365. Manchot and Gall prepare nickel carbonyl by mixing an aqueous solution of nickel sulphate in an atmosphere of carbon dioxide with potassium hydroxide and ethyl mercaptan; after some time the pressure in the vessel rises owing to the production of nickel carbonyl. The gaseous products are driven succes-

⁴⁶ Similar use of nickel carbonyl (0.3 per cent) is claimed in Brit. Pat. 259,314, July 10, 1925, to Asiatic Petroleum Co., Ltd., and Kewley. Cf. Tegner, *loc. cit.*

⁴⁷ Brit. Pat. 260,639, May 2, 1925, to the Badische Co.; *Chem. Abst.*, 1927, **21**, 3430.

⁴⁸ Brit. Pat. 260,640 to the Badische Co.

⁴⁹ The mixtures described in this paragraph appear to be covered by Can. Pats. 262,600, and 262,601, both of July 13, 1926, to Müller-Cunradi and Kossuth, and to Mittasch and Müller-Cunradi, respectively.

⁵⁰ U. S. Pat. 1,679,256, July 31, 1928, to Müller, Frankenburger and Grassner (to the I. G.).

⁵¹ Job and Reich, *Compt. rend.*, 1923, **177**, 1439.

⁵² *J. Chem. Soc., Abst.*, 1924 (i), 154; in the same connection, see Job and Reich, *Compt. rend.*, 1924, **179**, 330; *Chem. Abst.*, 1925, **19**, 236.

sively through an aqueous suspension of mercury acetate and a calcium chloride tube, after which the carbonyl is condensed in acetone-carbon monoxide. The solution is again treated with carbon monoxide and the process repeated. Even better results are obtained by the action of carbon monoxide on nickel sulphate mixed with potassium hydroxide and hydrosulphide. If nickel sulphate is replaced by iron sulphate, the production of small amounts of a volatile iron carbonyl is observed. With cobalt salts a marked absorption of carbon monoxide occurs, but a volatile cobalt carbonyl is not produced; the action may be utilized for the detection of small amounts of nickel in cobalt salts.⁵³

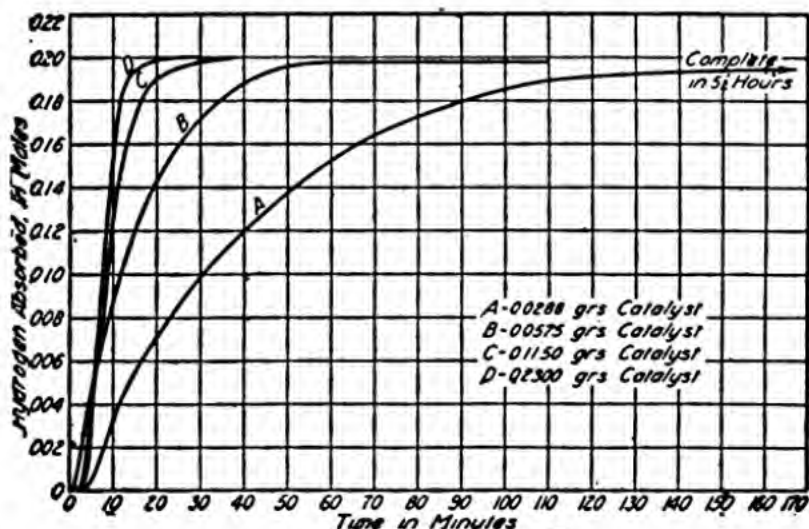


FIG. 25a.

1366. Experiments by Carothers and Adams (see Fig. 25a) on the effect of various amounts of catalyst upon the speed of reduction of a standard amount of benzaldehyde (see Chap. XIX, page 212) gave results showing the high activity of platinum-oxide platinum black. All factors remained constant except the amount of catalyst. It is remarkable how rapidly such an extremely small amount of platinum catalyst will cause the reduction of benzaldehyde to take place, providing ferrous chloride is present. In each of the experiments, 21.2 g. of benzaldehyde was dissolved in 50 cc. of alcohol, and 1 cc. of aqueous 0.1 M ferrous chloride was added. When 0.23 g. of catalyst was used, the reduction was complete in 23 minutes, with 0.115 g. in 34 minutes, with 0.0575 g. in 60 minutes, and with 0.0288 g. in 5.5 hours. The catalyst in each of these experiments was taken from a single sample.⁵⁴

⁵³ Ber., 1929, 62B, 678; Brit. Chem. Abst., 1929, 526A.

⁵⁴ J. Am. Chem. Soc. 1923, 45, 1071.

CHAPTER XIV

HYDROGENATION IN ORGANIC CHEMISTRY

CHIEFLY NON-INDUSTRIAL

1400. At the outset we said that we would not limit our subject-matter to catalytic hydrogenations in the strictest sense of the term, namely, to simple additive reactions. Catalytic reactions in which molecular hydrogen takes an active part, and some cognate reactions will be dealt with in this section on hydrogenations in organic chemistry. The commonest of these involve additions of hydrogen at an unsaturated carbon to carbon linkage, acetylenic or ethylenic. But there are other unsaturated linkages, though we do not habitually think of them as such.

1401. For example, $C:O$, $C:N$, $C\equiv N$ are all susceptible of hydrogenation. Probably the reason why the unsaturated character of these linkages is not obvious is because, unlike the acetylenic and ethylenic linkages, they yield, on hydrogenation, bodies which do not belong to the same class as the parent substances. Thus while an olefine hydrocarbon on hydrogenation yields a paraffin hydrocarbon, a nitro compound yields an amine, a ketone a secondary alcohol or a hydrocarbon and so on. In addition to hydrogenation of unsaturated linkages there are other catalytic reactions with molecular hydrogen with which we shall deal. For example, there is an important development in dehalogenations, by catalytic hydrogenation; again, sometimes, the result of an attempt to hydrogenate is a breaking up of the molecule with hydrogenation of the fragments.

1402. The quantity of research done on catalytic hydrogenation is prodigious and the literature is extremely voluminous. It is, therefore, from necessity rather than from choice that our presentation takes the form of an indication of work done and of an index of sources rather than of an exposition of the subject. Indeed, notwithstanding the vast amount of labor expended, but few generalizations have emerged. Those tentatively put forward have proved somewhat unstable: what was dogma yesterday is but pious opinion to-day and risks being heresy to-morrow. At present we are still in the stage of hunting facts, of amassing data. Pitfalls await the feet of him who enters the fields with blind confidence in the guidance of *a priori* deductions.

1403. It is true that we know that certain points of attack for hydrogenation in a molecule will surrender more easily than others. Thus, an unsaturated nitro-compound will usually be hydrogenated to an unsaturated amine more readily than to a saturated nitro-compound. But nitrostyrene, phenylnitro-

ethylene, is an exception. An attempt to hydrogenate it in alcohol or acetic acid solution leads to saturation without the nitro group being affected.¹

1404. With present-day knowledge of catalysts almost any unsaturated linkage can be hydrogenated catalytically. But not every catalyst will produce the same result and, what is important, the products of catalytic hydrogenation are sometimes quite different from those obtained by other methods, and even more often, when the possibility exists, they are geometric isomerides of the latter.

1405. It has been usual to arrange catalytic operations in categories of processes. Thus all hydrogenations over nickel in the vapor phase have been classed together for purposes of exposition, while hydrogenations in the liquid phase are treated in a different section. For readers who are chiefly interested in catalysis as such this arrangement is admirable.

1406. We feel, however, that most of our readers will wish to know how a particular hydrogenation can be effected. Therefore, all methods giving the same result should be grouped together, no matter how diverse the techniques.

1407. This dictates the classification either under the head of the product or of the parent substance. We have adopted the latter method: the hydrogenations described in this section are arranged according to the substances to be hydrogenated. This is true, in a general way, within the subsections.

1408. The division into subsections, however, was dictated by considerations of convenience. Sometimes the general class to which a substance belongs causes it to be allotted to a particular subsection. Thus all compounds with an acetylenic linkage will be found in a special subsection: the same is true of terpenes and compounds conveniently associated with them. In other cases the division into subsections has been made according to the results attained. Thus we have a section devoted to hydrogenation of ring nuclei of carbocyclic compounds, another to hydrogenations affecting nitrogen linkages, and a third to dehalogenations.

1409. In the matter of nomenclature we expect to be charged with inconsistency and we, hereby, enter a plea of confession and avoidance. In general, we have used the nomenclature of the source, except sometimes in the matter of spelling. In this way we hope that we have minimized error in our record.

1410. Nomenclature in organic chemistry is almost a professional specialty. We confess that we are not experts in that specialty and it is with some trepidation that we carefully transcribe (and proof-read) for example, that:

2-methoxy-4 : 6-diphenyl-3 : 3-dimethyl-3 : 4-dihydro-1 : 2-pyran is hydrogenated to 2-methoxy-4 : 6-diphenyl-3 : 3-dimethyltetrahydropyran; and

ethyl β -methyl- Δ^2 -tridecene- $\alpha\alpha$ -dicarboxylate to ethyl β -methyltridecane- $\alpha\alpha$ -dicarboxylate.

With pencil and paper we could work out those formulæ. But when a decision is sought between the Greek letters and the "arabic" numerals, we prefer the safety of a ringside seat to the precarious dignity of the referee's office.

¹ Only one atom of hydrogen is taken and 2 molecules condense (see para. 2543).

1411. We count ourselves fortunate not to have encountered, in preparing this book, the following: "5 B-1 : 1 : 22, 2 : 2 : 15, 3 : 3 : 8, 9 : 9 : 14, 16 : 16 : 21, *cyclo*-hexacosa- $\Delta^{4:6:10:12:17, 19:23:25}$ octene," or "hexar-3, 4-hexar'-2, 3-hexar''-2, 3-hexar; 4', 5'-hexar; 4'', 5''-hexar."² Even with the aid of several pencils and a quire of paper we doubt our ability to decode these cryptograms and to discover in both these names synonyms for 9, 10-diphenylene phenanthrene. A glance at the "*System der organischen Verbindungen*," recently published by the German Chemical Society as a guide-book to Beilstein, will afford some idea of the complexity of the nomenclature.

STERIC HINDRANCE: GEOMETRIC ISOMERISM

1412. Recently hydrogenation has begun to be applied to the investigation of geometric isomerism. Vavon seems to be the pioneer of this work.³ This line of inquiry is somewhat foreign to the purpose of this book. For this reason and because of the difficulty of presenting the results in a succinct form we shall content ourselves with a few examples and some references. The Zalkind (Sal-kind) and Ott articles are somewhat polemical.

1413. Orthopropylphenol.⁴ Hydrogenation of orthopropylphenol with platinum-black catalyst in acetic acid yields a mixture of orthopropylcyclohexanols with the *cis*-form predominating. This *cis*-compound oxidized by chromic acid mixture gives orthopropylhexanone whose oxime, hydrogenated with platinum-black gives orthopropylcyclohexyl- β -hydroxyl amine.

1414. The semicarbazone of the same ketone gives, on hydrogenation in hydrochloric acid with platinum-black, the hydrochloride of the semicarbazide.

1415. Isopropylphenol.⁵ The influence of the isopropyl group is less marked in the *para*- than in the *ortho*-position, and the difference in reaction velocities between the *cis*- and *trans*-forms of *p*-isopropylcyclohexanol is considerably smaller than between the *cis*- and *trans*-forms of 2-isopropylcyclohexanol (*loc. cit.*). *p*-Nitroisopropylbenzene is reduced by hydrogen more rapidly than the *o*-isomeride, affording an 80 per cent yield of *p*-isopropylaniline, converted by the diazo reaction into *p*-isopropylphenol (yield 65 per cent). Hydrogenation of the phenol in acetic acid in presence of platinum-black is also more rapid than with the *o*-isomeride, and affords a mixture consisting of 1 part of isopropylcyclohexane and 2 parts of a mixture of the *cis*- and *trans*-forms of 4-isopropylcyclohexanol in approximately equal proportions. The same mixture of alcohols is obtained by hydrogenation of 4-isopropylcyclohexanone affording, on hydrogenation in dilute hydrochloric acid in presence of platinum-black, β -4-isopropylcyclohexylhydroxylamine; the semicarbazone, similarly affords 4-isopropylcyclohexylsemicarbazide, in ether or acetic acid in presence of platinum-black. Hydrogenation of the ketone in acetic acid containing hydrochloric acid affords a mixture in which the *cis*-4-isopropylcyclohexanol preponderates, the influence of the medium being thus manifested when steric hindrance is less marked.⁶

1416. Hydrogenation of 2-isopropylcyclopentanone, in presence of platinum-black, in acetic acid containing 10 per cent of hydrochloric acid affords a mixture of 2-isopropylcyclopentanols in which the *cis*-isomeride predominates, but not to the extent observed in the case of the 2-isopropylcyclohexanols.⁷

² Patterson, *J. Am. Chem. Soc.*, 1928, **50**, 3074.

³ Vavon: Method for determining the *cis-trans*-isomerism in cyclic compounds. *Bull. soc. chim.*, 1926 [iv] **39**, 666. Application of catalytic hydrogenation results interpreted by the theory of steric hindrance; *idem. Rev. gén. sci.*, 1924, **35**, 505, contains 65 references.

⁴ Vavon and Anziani, *Bull. Soc. chim.*, 1927, **41**, 1638; *Chem. Abst.*, 1928, **22**, 1334.

⁵ Vavon and Callier, *Bull. Soc. chim.*, 1927, **41**, (iv), 677.

⁶ *Brit. Chem. Abst.*, 1927, 455A.

⁷ Vavon and Apchie, *Bull. Soc. chim.*, 1928, **43**, (iv), 667.

1417. Cis- and Trans- Forms of Borneol.⁸ *d*-Borneol prepared from camphor hydrogenated in acetic acid in presence of very active platinum-black gave more than 90 per cent *l*-isoborneol; when the absorption of $1\frac{1}{2}$ molecules hydrogen had taken place. When 2 molecules were absorbed, $C_{10}H_{18}$, the hydride of camphene, was formed, the *l*-isoborneol being dehydrated then hydrogenated. The yield was about 5 per cent *d*-borneol and 95 per cent $C_{10}H_{18}$.

1418. *l*-Isoborneol must be the *cis*-form, *d*-borneol the *trans*-form, because more of the *cis*- than of the *trans*-form is produced in hydrogenation of a ketone, and the *cis*-form is more slowly reactive than the *trans*-form, which statements apply to the iso-bornyl and to the bornyl series respectively. This differentiation is borne out by the other observations cited in the article.

1419. Differentiation of Cis- and Trans-Ethylenic Compounds by Catalytic Hydrogenation. Paul and Schniedewitz⁹ find that, when hydrogenated in alcoholic solution in presence of palladium (from palladous hydroxide) on barium sulphate or on calcium carbonate, *cis*-ethylenic compounds are invariably more readily reduced than the corresponding *trans*-compound. The work was done on maleic and fumaric acids, citraconic and mesaconic acids, oleic and elaidic acids, *cis*- and *trans*-cinnamic acids.

1420. Synthesis of Cis-ethylenic Compounds. Δ^a -Pentenoic acid hydrogenated in presence of colloidal palladium yields a Δ^a -pentenoic acid. Δ^a -Hexenoic acid when reduced in presence of colloidal palladium yields a Δ^a -hexenoic acid. Since these acids are different from the stereoisomeric acids already known, and these latter probably have the *trans*-configuration, it is probable that the acids here described have the *cis*-configuration. Reduction of phenylacetylenol in presence of colloidal palladium yields an allocinnamyl alcohol, b.p. $120.5^\circ/13$ mm. (phenylurethane, m.p. 89.5°), thus differing from ordinary cinnamyl alcohol. Support is thus found for the generalization that partial reduction of acetylenic compounds yields *cis*-ethylenic derivatives. (Bourguet and Yvon, *Compt. rend.*, 1926, **182**, 224).

REFERENCES ON STEREOISOMERISM

1421. v. Auwers and Schmelzer. Determination of the configuration of space isomeric hydroaromatic compounds (prepared by different methods of hydrogenation). *Sitzb. Ges. Beförderung gesamten Naturwissenschaften Marburg*, **62**, No. 4, 113; *Chem. Zentr.*, **1927**, II, 1562; full abstract in *Chem. Abst.*, 1928, **23**, 4486.

1422. Ott and Schröter. Semi-hydrogenation of the acetylenic linkage and dependence of the geometrical compound so formed on the rate of reaction. *Ber.*, 1927, **60B**, 624; *Brit. Chem. Abst.*, **1927**, 441A. The laws governing hydrogenation of acetylenic linkage not stereochemical: the course of the change is a question of energy.

1423. Salkind (Zalkind). Formation of geometrical isomerides by reduction of acetylenic glycols. *Ber.*, 1927, **60B**, 1125; *Chem. Abst.*, 1927, **21**, 2459; *Brit. Chem. Abst.*, 1927, 643A, answers Ott and Schröter.

1424. Ott, *Ber.*, 1927, **61B**, 2119; *Brit. Chem. Abst.*, **1928** 1351A. Ott (with Behr and Schröter), *Ber.*, **61B**, 1928, 2124; *Chem. Abst.*, 1929, **23**, 385; *Brit. Chem. Abst.*, **1929**, 1350A (both abstracts full).

1425. Catalytic Hydrogenation of Conjugated Double Bonds.¹⁰ It is well known that conjugated double bonds,



are more easily accessible to hydrogenation than the isomeric nonconjugated systems and react especially at the 1 : 4 position. The question whether this fact is true only for nascent hydrogen or also holds for catalytic hydrogenation was raised in connection with the cata-

⁸ Vavon and Peignier, *Bull. Soc. chim.*, 1928, **39**, 924.

⁹ *Ber.*, 1927, **60B**, 1221.

¹⁰ Vavon and Jakes, *Compt. rend.*, 1926, **183**, 299; *Chem. Abst.*, 1926, **20**, 3447; see further: Vavon, *Bull. Soc. chim.*, 1927 [iv] **41**, 1598; *Brit. Chem. Abst.*, **1928**, 150A.

lytic hydrogenation of carvone, which proceeds abnormally. To answer it material for experiment was selected in such a way that in every case the capacity for taking on hydrogen could be compared between similarly constructed or isomeric compounds with and without conjugation: styrol with cinnamic acid and benzalacetone; allyl acetic acid with dimethyl acrylic acid, etc. It turned out that the presence of a conjugated system exercised no important influence, and, with further experiments, that the 1:4 position is not accessible to catalytic hydrogenation. The latter is clearly different from the action of nascent, that is, atomic hydrogen. It should be noted, however, that the materials of experiment include only unlike conjugated systems: —C=C—C=O ; moreover, in styrol, which Vavon and Jakes mention as conjugation-free, the presence of a crossed conjugation may be assumed.

REFERENCES TO HYDROGENATION OF CONJUGATED DOUBLE BONDS

1426. Hydrogenation (non-catalytic) of conjugated compounds. Evans and Farmer, *J. Chem. Soc.*, **1928**, 1644. Discussion and experiment: Hydrogenation of crotylidene acetone, sorbic acid, ethyl muconate.

1427. See also: Farmer, Lavois, Swits, and Thorpe, *J. Chem. Soc.*, **1927**, 2937; *Chem. Abst.*, 1928, **22**, 941; Lebedev and Yakubchik, *J. Chem. Soc.*, **1928**, 823 and *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 981; *Brit. Chem. Abst.*, **1928**, 613A; *Chem. Abst.*, 1928, **22**, 4460. *Idem*, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 793; *Brit. Chem. Abst.*, **1928**, 968A; *Idem*, *J. Chem. Soc.*, 1929, 220; *Chem. Abst.*, 1929, **23**, 2432; Nishimatsu and Kimura. Catalytic reduction of β -naphthol. *Seisagint, Y. Osaka, Chem. Inst. Dept. Science, Kyoto Imp. Univ.*, **1927**, 203; *Chem. Abst.*, 1928, **22**, 1085.

1428. A Catalytic Method of Hydrogenation, without Free Hydrogen.¹¹ The material to be hydrogenated is dissolved in a suitable solvent in a stout-walled bottle, a small amount of a solution of palladium chloride or platinum chloride is added to act as a catalyst, and then the calculated amount of calcium hydride is added gradually, the flask being stoppered and well shaken. This method was successfully used for the reduction of benzaldehyde, nitrobenzene, and benzylidene-acetone.

¹¹ Nivière, *Bull. Soc. chim.*, 1921 (iv), **29**, 217; *J. Chem. Soc.*, 1921, **119** and **120**, ii, 391.

CHAPTER XV

HYDROGENATION OF ACETYLENIC LINKAGES

HYDROCARBONS

1500. Hydrogenation of Acetylene. Acetylene is hydrogenated to ethane by passage over a cobalt catalyst at 180°C . Liquid hydrocarbons are formed in small quantity and more abundantly at 250°C . [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), 4, 352.]

1501. At 130° over light purple copper, or at 180° over copper of clear red hue, in each case with excess of hydrogen, ethane and liquid hydrocarbons are produced. With excess of acetylene at 180° condensation occurs with production of a mixture of unsaturated and aromatic hydrocarbons (benzene, styrene, etc.), with some ethane and more ethylene, propylene and butylene. The copper swells up to an extraordinary extent, forming a light, fluffy, felted mass of filaments. This product has been named *cuprene*. It is a hydrocarbon with metallic copper disseminated through it. The empirical formula is C_7H_4 . It is perhaps hexaphenyl-cyclohexane, $\text{C}_6\text{H}_4(\text{C}_6\text{H}_5)_6$. [Sabatier and Senderens, *Bull. Soc. Chim.*, 1899 (3), 21, 530; *Compt. rend.*, 1900, 130, 250; Sabatier, 3rd Congress on Acetylene, Paris, 1900, 345, and 4th Cong. App. Chem., Paris, 1900, 3, 134.] For other investigations on cuprene see: Erdmann and Köthner, *Z. anorg. Chem.*, 1898, 19, 48; Alexander, *Ber.*, 1899, 32, 2381; Kaufmann and Schneider, *Ber.*, 1922, 55B, 267. Cf. Ellis, *Synthetic Resins and their Plastics*, p. 63.

1502. With iron catalyst, above 180° , acetylene gives large amounts of colored hydrocarbons (higher ethylene hydrocarbons, aromatic hydrocarbons and traces of saturated hydrocarbons) resembling natural petroleum of Canada. [Sabatier and Senderens, *Compt. rend.*, 1900, 130, 1628.]

1503. With nickel catalyst and excess of hydrogen acetylene is hydrogenated completely to ethane. If the acetylene is in excess, the metal heats up, liquid aromatic and hydro-aromatic hydrocarbons are formed. The larger the excess of acetylene, the greater the heat developed, up to incandescence, with partial polymerization to benzene. [Sabatier and Senderens, *Compt. rend.*, 1899, 128, 1173.]

1504. With (colloidal) palladium catalyst shaken with water acetylene gives chiefly ethylene, up to 80 per cent. [Paal and Hohenegger, *Ber.*, 1915, 48, 275.]

1505. Platinum-black (at room temperature) yields ethane, with ethylene as intermediate. [Von Wilde, *Ber.*, 1874, 7, 352.]

1506. Progressive Hydrogenation of Acetylene.¹ Since the adsorption of acetylene is less pronounced with colloidal platinum (sodium protalbinat protective) than with colloidal palladium, it was anticipated that the conversion of acetylene into ethylene in presence of the former would be more complete than in presence of the latter; actually the reverse was the case. When equal volumes of acetylene and hydrogen were used the product contained about half the calculated amount of ethylene, in addition to a considerable amount of ethane and some unchanged acetylene. In all cases, hydro-

¹ Paal and Schwarz, *Ber.*, 1915, 48, 1202-1207.

genation in presence of colloidal platinum proceeded more slowly than in presence of colloidal palladium.

1507. Platinum-black at room temperatures catalyzes the hydrogenation of acetylene to ethane, but the life of the catalyst is short. At room temperature spongy platinum has no catalytic activity. Both forms at 180° C. produce results similar to those caused by the use of nickel.

1508. Some Ethylene Hydrocarbons Obtained by Semireduction of the Corresponding Acetylenes. [Bourguet, *Bull. Soc. Chim.*, 1927, 41, 1475-1479.] Reduction of acetylenes with hydrogen and colloidal palladium at room temperature gives only the corresponding olefine. The products are therefore in general purer than those previously described. Values following the boiling-points are, respectively, *d.* and *n_D*, both at the temperature given: 1-pentene, 32.5°, 0.644, 1.371 (20°); 2-pentene, 34.5°, 0.647, 1.375 (19°); 1-hexene, 64.5°-65°, 0.684, 1.393 (14°); 1-heptene, 94°-94.5°, 0.705, 1.404 (20°); 1-octene, 122°, 0.718, 1.408 (19°); 2-octene, 125°-126°, 0.725, 1.415 (20°); 1-nonene, 146°, 0.730, 1.414 (21°); 2-nonene, 148.5°, 0.738, 1.420 (21°). 1-Cyclohexyl-olefines: propene, 152° (following boiling-points not corrected), 0.808, 1.449 (21°); butene, 174 (b₁₄ 62°), 0.810, 1.450 (21°); pentene, 196° (b₁₄ 83°), 0.816, 1.454 (20°) (2-cyclohexylpentene, 198°-199° (b₁₈ 85°), 0.822, 1.458 (20°); hexene, 219° (b₁₈ 99°), 0.820, 1.457 (21°) (2-deriv., 221° (b₁₇ 102°), 0.823, 1.459 (21°)).²

1509. Industrial Hydrogenation of Acetylene to Ethylene. This is the initial step in the synthesis of ethanol. Ross, Culbertson and Parsons³ believe that the tendency to form ethane, when using an active nickel catalyst, is due to the high condensation of hydrogen at the surface of the metal. In confirmation of this, they were able to obtain an 80 per cent yield of ethylene by passing an equimolecular mixture of acetylene and hydrogen, in batch fashion, over a freshly reduced nickel catalyst.

1510. Karo obtains a good yield of ethylene by the use of a platinum group metal mixed with a base metal.⁴

1511. Ethylene from Acetylene. Ross⁵ effects the partial hydrogenation of acetylene to ethylene in the following manner: A metallic catalyst (e.g., nickel) is treated with hydrogen at a temperature not above 150° C. and then with acetylene, followed by a mixture of acetylene and hydrogen, the operation being conducted at 150° C., or lower.

1512. Controlled Hydrogenation of Acetylene to Produce Ethylene. Eldred and Mersereau⁶ state that catalytic hydrogenations in the vapor phase which tend to go too far for a given purpose may often be brought under control by dilution of the reacting vapors and gases with an inert gas. The procedure is particularly described for the production of ethylene from acetylene, a reaction whose greatest interest is due to the fact that it is a step in the synthesis of alcohol (ethanol). Without a diluent the hydrogen-acetylene mixture passed over a catalyst, such as nickel, reacts exothermically and energetically with the formation of indefinite mixtures of products. But, if the hydrogen-acetylene mixture be diluted with half or one-third its volume of carbon dioxide, the reaction proceeds smoothly with a good yield of ethylene.

1513. Controlled Hydrogenation of Acetylene.⁷ Though Lane has described, in general terms, a process for the production of compound gases, the method is specifically utilizable in the hydrogenation of acetylene to ethylene. The mixture of gases (hydrogen and ethylene) passes over catalyst disposed in relatively narrow metal tubes. These tubes are immersed in a fluid whose boiling-point is the desired reaction temperature. The tubes pass several times through this bath, and before each point of entry there is, in the tube, a valve permitting the gas mixture to be enriched in one or other of its constituents. In this way the violence of reaction which occurs with equimolecular pro-

² *Chem. Abst.*, 1928, 22, 1324.

³ *Ind. Eng. Chem.*, 1921, 21, 775.

⁴ Ger. Pat. 253,160.

⁵ U. S. Pat. 1,392,852, Oct. 4, 1921.

⁶ U. S. Pat. 1,308,777, July 8, 1919.

⁷ Brit. Pat. 10,724, 1911.

portions, and which tends to disruption with carbon deposit, is controlled. Owing, also, to the small size of the tube, the heat is quickly communicated to the bath fluid and is taken up as latent heat of vaporization.

1514. Catalytic Production of Ethylene. Acetylene is passed with an equal volume, or even with excess, of hydrogen in fine bubbles into an inert liquid (deca- or tetrahydronaphthalene) containing the catalyst (palladium or nickel on kieselguhr) in suspension, preferably at about 150° C. and under pressure if desired. Ethylene with very little ethane is produced.⁸

1515. Diethylacetylene to hexane. Diphenylacetylene to stilbene or dibenzyl.⁹

1516. Trimethylpropinmethane to trimethylpropylmethane. Platinum-black catalyst. [Graef, *Bull. Soc. Chim., Belg.*, 1925, **34**, 427.]

1517. α -Heptene, α -nanthylidene, to n -heptane. Gas phase: 170° C.: nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 87.] Over copper, below 200°, α -heptene slowly gives heptene, diheptene and triheptene and some n -heptane. [Sabatier and Senderens, *loc. cit.*]

1518. Phenyl-acetylene to ethyl-cyclohexane. Gas phase: 180°: nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 88.]

1519. Over copper at 190°–250° phenylacetylene gave ethyl-benzene, a little phenyl-ethylene and 50 per cent diphenyl-butane, a crystalline solid whose solutions fluoresce splendidly. [Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 88.]

1520. In acetic acid solution, with colloidal palladium catalyst, phenylacetylene is hydrogenated first to styrene, then to ethyl-benzene. [Kelber and Schwarz, *Ber.*, 1912, **45**, 1951.]

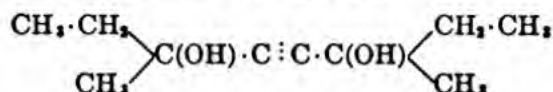
1521. Tolane (diphenylacetylene) to dibenzyl. Acetic acid solution: colloidal palladium catalyst. Stilbene is an intermediate product. [Kelber and Schwarz, *Ber.*, 1912, **45**, 1951.]

1522. Tolane diphenylacetylene, hydrogenated under various conditions of temperature, pressure and catalyst ratio. Paal's colloidal palladium catalyst. [Zalkind and Il'in, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 994–997, *Chem. Abst.*, 1927, **21**, 2267.]

1523. Diphenyl-diacetylene first to $\alpha\gamma$ -diphenyl-butadiene $\alpha\gamma$, then to $\alpha\gamma$ -diphenyl-butane. Acetic acid solution: Colloidal palladium catalyst. [Kelber and Schwarz, *Ber.*, 1912, **45**, 1951.]

OTHER COMPOUNDS

1524. Acetylene glycols with colloidal palladium catalyst hydrogenate in different ways: (1) 2, 5-dimethyl-hexine (3)-diol (2, 5), 1, 4-diphenyl-butine (2) diol (1, 4), dimethyl-di-ethyl-butine-diol, and dimethyl-octine-diol



add H₂ in one stage to give the ethylene diol.

1525. (2) Dimethyl-diphenyl-butine diol hydrogenates in two-stages giving first, the ethylene glycol and then the saturated glycol.

1526. (3) 2-methyl-4-phenyl-butine (3)-ol (2), (CH₃)₂C(OH)·C≡C·C₆H₅, takes up 2H₂, giving directly the saturated alcohol. [Sabatier. *Catalysis in organic chemistry*, 548.]

1527. With platinum- and palladium-black (method of Willstätter) the hydrogenation of acetylene glycols is also not the same for all, nor does it always follow the same path as hydrogenation of the same compounds with colloidal palladium.

⁸ Brit. Pat. 294,787, Aug. 27, 1927, to Johnson (from I. G. Farbenind., A.-G.), *Brit. Chem. Abst.*, 1928, 704B; French Pat. 651,037, Mar. 30, 1928.

⁹ Brit. Pat. 279,095, Oct. 14, 1926, to Corson.

1528. The glycols of the formula $RR' : C(OH) \cdot C : C \cdot C(OH) : RR'$ yield a mixture of the saturated glycol and the alcohol, $RR' : C(OH)CH_2 \cdot CH_2 \cdot CH_2 : RR'$. 2, 5-dimethyl-hexine (3) diol (2, 4) gives the saturated glycol.

1529. Dimethyl-diethyl-butene-diol (which takes up H_2 with colloidal palladium) adds $2H_2$. Dimethyl-diphenyl-butene-diol takes up first H_2 then yields the saturated glycol.

1530. Octadecane-diol (1, 8), $HOH_2C \cdot C : C \cdot CH_2 \cdot CH_2 \cdot C : C \cdot CH_2OH$ at 70° in alcohol gives a mixture of octane-diol (1, 8) and *n*-octyl alcohol.

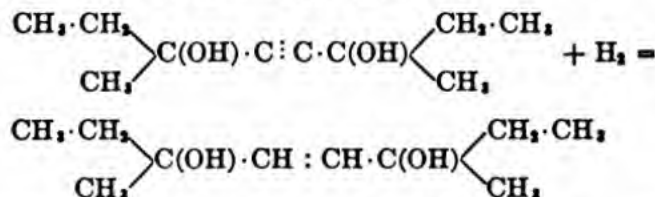
[Willstätter and Mayer, *Ber.*, 1908, **41**, 2199; Dupont, *Compt. rend.*, 1913, **156**, 1623; Zalkind, *J. Russ. Phys. Chem. Soc.*, 1914, **45**, 1875, *Chem. Abst.*, **8**, 1419; Zalkind and Markaryan, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 538, *Chem. Abst.*, **11**, 584; Zalkind and Kvapishvskii, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 688, *Chem. Abst.*, **9**, 2511; Lespieau, *Compt. rend.*, 1914, **158**, 1187], see para. 1535.

1531. 2, 5-Dimethylhexine (3)-diol (2, 5) to ethylene-diol. Liquid-phase: colloidal palladium catalyst. [Zalkind, *J. Russ. Phys. Chem. Soc.*, 1914, **45**, 1875, *Chem. Abst.*, **8**, 1419.]

1532. With platinum-black catalyst the 2, 5-dimethylhexine (3) diol (2, 4) gives the saturated glycol. [Zalkind, *loc. cit.*]

1533. 1, 4-Diphenyl-butene (2)-diol to 1, 4-diphenyl-butene (2)-diol. Liquid phase: colloidal palladium catalyst. [Zalkind, *J. Russ. Phys. Chem. Soc.*, 1914, **45**, 1875; *Chem. Abst.*, **8**, 1419.] With a platinum catalyst the saturated glycol is obtained.

1534. Dimethyl-octene-diol to dimethyl-octene-diol



Liquid phase in alcohol solution: colloidal palladium catalyst. [Zalkind, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2045; *Chem. Abst.*, **10**, 1355].

1535. Octadecane-diol (1, 8) to octane-diol (1, 8) and *n*-octyl alcohol. Alcohol solution: 70° : platinum-black catalyst. [Lespieau, *Compt. rend.*, 1914, **158**, 1187.]

1536. Tetraethylbutenediol $[(C_2H_5)_2C(OH)C:]_2$ to tetraethylbutenediol $[(C_2H_5)_2C(OH)CH_2]_2$. Ether solution: palladium or platinum-black catalyst. Tetraethylbutenediol was obtained as an intermediate. [Zalkind and Buistryakov, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 680.]

1537. Dimethyldiphenylbutenediol $[CH_3C_6H_5C(OH)C:]_2$ (2 isomers (a) m.p. 163° C., (b) m.p. 125° – 127° C.) to dimethyldiphenylbutenediol $[CH_3C_6H_5C(OH)CH:]_2$, 1 isomer from (a) and another from (b), and dimethyldiphenylbutanediol. [Zalkind and Kvapishvskii, *Ibid.*, 688.]

1538. Methyl-tertiary-butylethynylcarbinol ($\gamma\delta\delta$ -trimethylpentinene- γ -ol) $CCH_3 \cdot CCH_3(OH) \cdot C : CH$ to methyl-tertiary-butylvinylcarbinol $(CCH_3 \cdot CCH_3(OH) \cdot CH : CH_2)$. Methyl alcohol solution: nickel catalyst. [Wouseng, *Am. Chim.*, 1924, (x), **1**, 343.]

1539. 2-Methyl-4-phenyl-butene-3-ol(2) (δ -phenyl- β -methyl- Δ^7 -butene- β -ol, $HO \cdot C(CH_3)_2 \cdot C : C \cdot C_6H_5$) to 2-methyl-4-phenyl-butanol (β -phenylethylmethyl carbinol, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C(CH_3)_2OH$). Absolute ethanol solution: colloidal palladium: room temperature. [Zalkind, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2045.]

1540. 1-Butene-carboxylic acid to *cis*-1-butene-carboxylic acid.

1541. 1-Pentene-carboxylic acid to *cis*-1-pentene-carboxylic acid.

1542. Phenylacetylene alcohol to *cis*-cinnamyl alcohol. Colloid palladium catalyst. [Bourguel and Yvon, *Compt. rend.*, 1926, **182**, 224; *Chem. Abst.*, 1926, **20**, 2978.]

1543. Octadecane-dioic acid to suberic acid. Alcohol-ether solution: platinum-black catalyst: 4 days. [Lespieau, *Compt. rend.*, 1914, **158**, 1187.]

1544. Ambrettolic acid, 7-hexadecene-16-olic 1-acid (from muskseed oil) to juniperic acid, dihydroambrettolic acid.

1545. Lactone (b.p. 13 mm., 185°–190° C.) from muskseed oil with 17 members in the ring to a compound boiling under 13 mm. pressure, at 175°–180°: platinum sponge: glacial acetic acid solution. [Kirschbaum, *Ber.*, 1927, 60B, 902–909.]

1546. Behenolic acid by partial hydrogenation with nickel catalyst gives erucic acid.

1547. Stearolic acid by partial hydrogenation with nickel catalyst gives oleic acid. [Gonzalez, *Anal. Fis. Quím.*, 1926, 24, 156.]

1548. Phenylpropionic acid to cinnamic acid. Colloidal palladium catalyst. Unsatisfactory. [Paal and Schwartz, *Ber.*, 1918, 51, 640.]

1549. Partial Reduction of Phenylpropionic Acid.¹⁰ It has been noted that the hydrogenation of phenylpropionic acid and acetylene can be so controlled under certain conditions, using colloidal palladium as the catalyst, that the corresponding ethylenic compounds are the main products and that in the case of acetylene, colloidal platinum is less efficient, a mixture of ethylene, ethane, and unreduced acetylene being generally obtained. The hydrogenation of phenylpropionic acid by means of colloidal platinum gives a much lower yield of malenoid forms of cinnamic acid than when palladium is used, but no *n*-phenylpropionic acid could be detected under the conditions employed. The deficiency is largely due to the formation of indefinite by-products.¹¹

1550. By controlling the absorption of hydrogen, using colloidal palladium hydrosol, Paal and Hartmann hydrogenated phenylpropionic acid to cinnamic acid. Allocinnamic acid was most readily obtained, showing the ease of *cis*-addition. [*Ber.*, 1909, 42, 3930.]

1551. Tetrollic acid (methyl-acetylene carboxylic acid, $\text{CH}_3 \cdot \text{C} \equiv \text{C} \cdot \text{COOH}$), to butyric acid. Liquid phase: colloidal palladium catalyst. [Böeseken, van der Weide and Mom, *Rec. Trav. Chim. Pays-Bas*, 1915, 35, 260.]

1552. Tetrollic acid to crotonic acid. Colloidal platinum hydrosol: hydrogen absorption restricted: addition takes place in the *cis*-position, allocrotonic acid 63 per cent yield; ordinary crotonic acid 4 per cent yield. [Williams and James, *Aberystwyth Studies*, 1922, 4, 197.]

1553. Acetylene di-carboxylic acid treated in the same way underwent *trans*-addition with production of fumaric acid and no maleic acid. Further reduction to succinic acid went rapidly [*Ibid.*].

1554. Hydrogenation of Triple Bond. Formation of *Cis*-ethylenic Compounds. Hydrogenation of compounds containing acetylenic linkages, at low temperatures with colloidal palladium yielded *cis*-ethylenic compounds. Previously *trans*-isomers only or mixtures had been obtained by hydrogenation. Phenylpropionic acid gave *cis*-cinnamic acid. Tolane (diphenyl acetylene) gave iso-stilbene. Acetylene dicarboxylic acid gave malic acid. Tetrollic acid gave iso-crotonic acid. Tetramethylbutenediol gave *cis*-tetramethyl-butenediol.¹²

1555. Cyclohexylideneacetaldehyde to cyclohexylacetaldehyde. Nickel catalyst. [Rupe, Messner and Kambli, *Helv. Chim. Acta*, 1928, 11, 449.]

1556. Acetylenedialdehyde acetal to succindialdehyde acetal (which on treatment by an acid yields succindialdehyde). Skita's method: colloidal palladium catalyst. [Keimatsu and Yokota, *J. Pharm. Soc. Japan*, 1927, 542, 284.]

1557. Phenylpropargylaldehyde diethylacetal to *trans*-cinnamaldehyde diethylacetal. Palladium-charcoal catalyst.

1558. Piperonylpropargylaldehyde gave oily products.

1559. Piperonylacetaldehyde gave piperonyl propane.

1560. Phenylpropargylidene malonic acid in methanol gave an oily product, in acetic acid an oil, probably *cis-cis*-cinnamylideneacetic acid, and some cinnamylidene malonic acid; the sodium salt gave an oil, the pyridine salt *cis*-cinnamylidene malonic acid.

¹⁰ Paal and A. Schwartz *Ber.*, 1918, 51, 640–643.

¹¹ *J. Chem. Soc.*, 1918, Abst. i, 343.

¹² Bourguet, *Compt. rend.*, 1925, 180, 1753.

1561. Piperonylpropargylidene malonic acid apparently lost CO_2 , giving amorphous products: the pyridine and piperidine salts also gave unsatisfactory products; from the last *trans*-piperonylethylidene malonic acid was obtained and a small quantity of the *cis*-form. [Lohaus, *J. prakt. Chem.*, 1928, **119** (ii), 235.]

1562. Oenanthylidene-acetic acid (ethyl ester) to nonylic acid (ethyl ester, ethyl pelargonate). Gas phase: 180° : nickel catalyst. [Darzens, *Compt. rend.*, 1907, **144**, 328.]

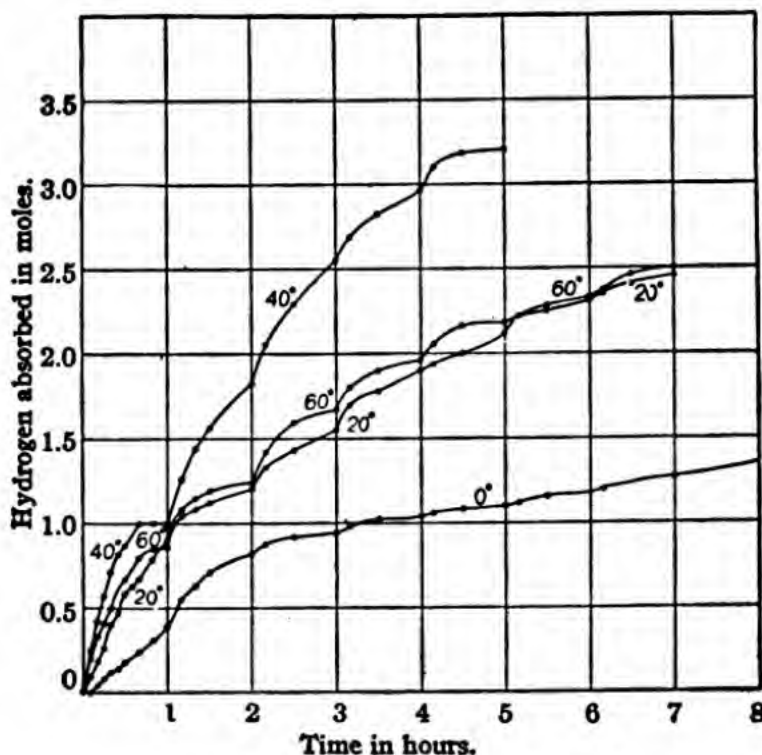


FIG. 25b.—SEE ALSO FIG. 25c, PAGE 210.

The effect of temperature on the reduction rate of furfural (Cf. Chap. XXVII, page 282) in 95 per cent alcohol, at 0° , 20° , 40° and 60° , with platinum black from $\text{PtO}_2 \cdot \text{H}_2\text{O}_4$ as catalyst, determined by Pierce and Parks. Increase in temperature from 0 to 40° causes a marked increase in the reduction rate of furfural, and at 60° , if sufficient catalyst is present, the initial reduction rate is much greater than at 40° . However, at 60° the catalyst is rendered inactive more readily than at 40° , so particularly if only a small amount of catalyst is present, the reduction will proceed faster at 40° than at 60° . 0.1 mol furfural, 0.122 g. catalyst and 1 cc. M/10 ferrous sulphate was used. (*J. Am. Chem. Soc.*, 1929, **51**, 3384.)

CHAPTER XVI

ETHYLENE HYDROCARBONS: ETHERS, ALCOHOLS, ALDEHYDES

HYDROCARBONS

1600. Rates of Hydrogenation of Aliphatic Ethylenic Compounds Alone and in Mixtures.¹ The rate of absorption of hydrogen by unsaturated ethylenic compounds in presence of platinum-black is, in general, a linear function of the time. The highest rate of absorption is exhibited by mono-substituted compounds, and as the number of substituents increases the rate declines. Mono-, tri-, and tetra-substituted derivatives absorb hydrogen at a uniform rate throughout the greater period of the action, but di-substituted compounds do so only during a shorter period of the action. In certain cases where more than one ethylenic linking is present, there are two well-defined rates of absorption. Negative substituents cause an abnormally slow velocity of absorption, while conjugation with an alicyclic or carbonyl residue tends to increase the rate.

In a mixture of two similarly substituted ethylenic compounds the components are hydrogenated concurrently, but when dissimilarly substituted, the components are hydrogenated consecutively. When the two substances are substituted to different degrees they are attacked successively. In binary mixtures containing a monosubstituted compound, this maintains its characteristic and more rapid rate of absorption, and when a tetra-substituted derivative is present this also preserves its own rate of absorption. Di- and tri-substituted compounds in admixture exhibit either a lower or a higher rate of absorption than when hydrogenated alone, so that the two rates tend to approach one another.

These results may be utilized to determine the degree of substitution of an ethylenic compound by comparison of its rate of hydrogenation in the pure state and when in admixture with a typical substituted unsaturated compound, such as allyl alcohol, etc.²

1600a. Reaction of Atomic Hydrogen with Ethylene, etc. Ethylene with an excess of hydrogen and in the presence of excited mercury atoms gives practically entirely ethane. If, however, relatively high concentrations of ethylene are used, the saturated hydrocarbons formed are more complex. The reaction may also furnish liquid condensation products of the composition $(CH_2)_n$. Methane is also formed and is acted on by hydrogen atoms under the influence of excited mercury atoms. The effect of atomic hydrogen on the saturated hydrocarbons varies with the molecular weight, being the more rapid the greater is the molecular weight. The velocity of the reaction between ethylene and hydrogen is accelerated considerably by increase in the hydrogen atom concentration, other things being equal. The reaction is therefore started by hydrogen atoms. With large excess of ethylene, acetylene is formed in considerable quantity, but with excess of hydrogen no acetylene is formed.^{3a}

¹ Lebedev, Kobliansky and Yakubchik, *J. Chem. Soc.*, **1925**, 418.

² *J. Chem. Soc., Abst.*, 1925, i, 350.

^{3a} Taylor and Hill, *Z. physikal. Chem.*, 1929, B, 2, 449-450. *Brit. Chem. Abst.*, **1929**, 655A.

1601. Ethylene. Ethylene is readily and sharply hydrogenated over nickel, in the presence of an excess of hydrogen, ethane being the sole product. The reaction commences at 30° C. and is rapid round 150° C. For the preparation of pure ethane, an excess of ethylene must be used. The result is a mixture of ethane and residual ethylene; the latter can be removed by absorption in bromine water. [Sabatier and Senderens, *Compt. rend.*, 1927, **124**, 1359.] Above 300° the ethylene is decomposed, carbon is deposited and a mixture of methane and higher paraffins is produced. [Sabatier and Senderens, *loc. cit.*]

1602. Industrial Hydrogenation of Ethylene. Ethane for use in refrigerating machines has been produced by the hydrogenation of ethylene. The ethylene was obtained by dehydration of ethanol. Such ethylene contains much catalyst poison, ether, aldehyde, isoprene, sulphur compounds, and others. These were removed in three stages: (1) compression to 50 atmospheres causing condensation of the first group of poisons; (2) treatment with lead acetate solution; (3) scrubbing with sulphuric acid. The purified ethylene and hydrogen, in equal volumes, are passed, at 200°, over a nickel catalyst contained in tubes. For a velocity of 2 cu. m. an hour, to produce a gas containing 80 per cent of ethane, the tubes are 1 m. long and 0.075 m. in diameter. The effluent gas is compressed to 30–40 atmospheres, in the presence of a nickel catalyst supported on pumice. [Sprenst, *J.S.C.I.*, 1913, **32**, 171.]

1603. Cobalt also catalyzes the hydrogenation of ethylene, but is more rapidly put out of action than nickel and presents no advantages. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 344.]

1604. Another method of hydrogenating ethylene at atmospheric pressure with a nickel catalyst is that used by Rather and Reid. [*J. Amer. Chem. Soc.*, 1915, **37**, 2115.] Ethylene and hydrogen, the latter in excess, are bubbled through a saturated hydrocarbon carrying in suspension a nickel catalyst. For details see paras. 723–728.

1605. Copper catalyzes the hydrogenation of ethylene at 180° C. [Sabatier and Senderens, *Compt. rend.*, 1902, **134**, 1127.] Constable [*Z. Elektrochem.*, 1929, **35**, 105] reports two series of experiments on the hydrogenation of ethylene at 0°, 100° and 200°, in presence of a copper catalyst, which was prepared by the repeated reduction of copper oxide with hydrogen. In the first, equal volumes of hydrogen and ethylene were employed at pressures of 19, 38, 50, and 76 cm.; and in the second, the volumes of the reacting gases were varied but the pressure was kept constant at 76 cm. The first series showed that the surface of the catalyst was almost saturated with the gases at 0°, but was partly saturated at 100° and was very unsaturated at 200°. According to the second set, and with the particular catalyst used, the rate of production of ethane was at a maximum at 0° when the reaction mixture contained 18 vol.-% of ethylene; at 100°, 42%; and at 200°, approximately 50%. The superficial area of the catalyst was ascertained by means of an interference method after coating the catalyst with a film of oxide by direct oxidation. The interference method was also employed to investigate the nature of the gases adsorbed by the catalyst. At 0° much of the surface appeared to be covered with a unimolecular layer of hydrogen, while much of the remaining part was covered with ethylene. [*Brit. Chem. Abst.*, 1929, 520A.]

1606. In the liquid phase, colloidal palladium is an efficient catalyst for the hydrogenation of ethylene [Paal and Hartmann, *Ber.*, 1915, **48**, 984], and is superior in this respect to colloidal platinum [Paal and Schwarz, *Ber.*, 1915, **48**, 994].

1607. With excess of hydrogen ethylene can be reduced to ethane by Ipatiev's method: 60 atmospheres hydrogen: 180° C.: copper oxide catalyst. Nickel oxide catalyst causes breakdown to methane. [*Ber.*, 1909, **42**, 2089.]

1608. Pease and Stewart¹ find that metallic calcium or calcium hydride will catalyze the hydrogenation of ethylene. They are doubtful whether the reaction of the hydrocarbon with the hydride is an intermediate stage.

1609. Catalytic Reactions of Ethylene. Walker [*J. Physical Chem.*, 1927, **31**, 961–996.] The products obtained when ethylene is passed over various solid catalysts have

¹ *J. Am. Chem. Soc.*, 1925, **47**, 2763.

been investigated. Ethylene is stable towards heat at 600° C.; at 615° C. decomposition commences in a Jena glass tube. Polymerization to a colorless and to a brown oil occurs accompanied by decomposition into acetylene, hydrogen, methane, and carbon, and by hydrogenation to ethane. Acetylene is less stable than ethylene, decomposing above 400°. Mixtures of equal quantities of acetylene and ethylene at 600° in contact with Jena glass yield a mixture of the polymerized initial constituents. Silica gel, silica gel and borax, silica gel and calcium hydroxide, borax, calcium silicate, and zinc oxide are all inert towards ethylene up to 600° C. Complete reduction by ethylene of ferric oxide, zinc oxide, and lead monoxide occurs at 500°, 800–900°, and 600° C. respectively. Over the range 100°–500° C., ethylene is polymerized by sodium to a colorless oil and is decomposed to carbon, hydrogen, and methane. Ethane, carbides, and hydrides are also formed. With nickel at 400° C., no polymerization occurs but the ethylene is decomposed into hydrogen and acetylene. Rapid carbonization at 400° C., and complete decomposition at 545° C., take place in presence of cobalt. No liquid polymerides are formed. Iron polymerizes ethylene at 360° C. to a colorless oil and decomposes it slowly into carbon and hydrogen. At 425° C. decomposition is practically complete. A small percentage of potassium hydroxide does not increase the polymerization brought about by the iron. Chromium oxide does not promote activity of the iron. Increased pressure does not permit the continuous formation of liquid polymerides owing to carbon deposition. Pressure studies show that methane is produced from ethylene by fission of the two carbon atoms to yield two CH₂ groups which are subsequently hydrogenated.⁴

1610. Mulliken and Moore reduce ethylene to ethane by hydrogen in the presence of a catalyst which is cooled in order to remove the heat generated by the reaction.⁵

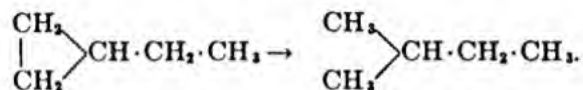
1611. Propylene to propane. From cold to 200° : nickel catalyst : with hydrogen in excess. With propylene in excess, at higher temperatures, especially above 290°, there is condensation to liquid hydrocarbons, with petroleum odors. At still higher temperature there is deposit of carbon with "cracking" of the propane. [Sabatier and Senderens, *Compt. rend.*, 1902, **134**, 1127.]

1612. With a copper catalyst propylene can be hydrogenated at 180°. [Sabatier and Senderens, *loc. cit.*]

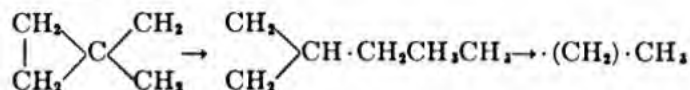
1613. The hydrogenation may also be carried out with platinum-black as catalyst, though less satisfactorily than with nickel. Carbonization of the catalytic surface interferes with the activity. [Sabatier and Senderens, *Compt. rend.*, 1900, **131**, 40.]

1614. Amylene to pentane. Liquid phase: colloidal platinum catalyst. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276.] The same with platinum-black.

1615. Ethyl-trimethylene to iso-pentane. Gas phase: nickel catalyst. [Rozanov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 168; *Chem. Abst.*, **11**, 454.]



1616. Spirocyclane to pentane. Gas phase : platinum catalyst. Ethyl trimethylene is also formed.



With palladium ethyl trimethylene only, and with nickel at 200° pentane only are formed. [Zelinsky and Scherbak, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 880.]

1617. Treatment of a product containing cyclohexanespiro-3-bromocyclohexane with zinc-dust and alcohol gave a hydrocarbon mixture which with hydrogen and col-

⁴ *Brit. Chem. Abst.*, **1927**, 837A.

⁵ U. S. Pat. 1,107,696, Aug. 18, 1914.

loldal palladium was debrominated to cyclohexanespirocyclohexane. The mixed hydrocarbons (6 g.) were shaken in an atmosphere of hydrogen for eight hours with 2.5 cc. of a 10 per cent solution of palladium chloride, 2.5 cc. of a 10 per cent solution of gum arabic in water, 5 cc. of water, and enough alcohol to give a clear solution. The initial pressure of gas was 1070 mm.; this fell gradually to 815 mm. The product was isolated by distillation in steam and extraction of the distillate with ether. [Norris, *J. Chem. Soc.*, 1926, **129**, 252.]

1618. Vinyl-trimethylene to ethyl-trimethylene. Liquid phase : cold : 35 atmospheres : palladium chloride (which undergoes reduction) as catalyst. [Filippov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 469.]

1619. Trimethylethylene to isopentane. Gas phase : 150° : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1902, **134**, 1229.]

1620. Hexene (2) to hexane. Gas phase : below 160° (at above 200°, and still more at 300° the hydrocarbon chain breaks) : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1902, **134**, 1127.]

1621. Methyl-ethylpropylenemethane to methyl-ethylpropylmethane. Platinum-black catalyst. [Graef, *Bull. soc. chim. Belg.*, 1925, **34**, 427.]

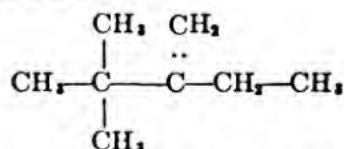
1622. Preparation of isomeric heptanes (by hydrogenation of the heptenes). Edgar, *Organic Symposium*, Columbus, Ohio, 1927.]

1623. Caprylene (octene) to octane. Gas phase : below 160° : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1902, **134**, 1127.]

1624. Nonene (2) to nonane. Gas phase : 160° : nickel catalyst. [Clark and Jones, *J. Amer. Chem. Soc.*, 1915, **37**, 2536.]

1625. 2-Ethyl-5-methyl-hexene to 2, 5-dimethyl-heptane (b.p. 135°). Gas phase : 160° : nickel catalyst.

1626. 2, 2-Dimethyl-3-methene



to 2, 2, 3-trimethylpentane. [Clark and Jones, *J. Am. Chem. Soc.*, 1912, **34**, 170; Clark and Beggs, *ibid.*, 54.]

1627. Methyl-propyl-octene to methyl-propyl-octane. Gas phase : below 160° : nickel catalyst. [Murat and Amouroux, *J. Pharm. Chim.*, 1912, (7), **5**, 473; *Chem. Abst.*, **7**, 1494.]

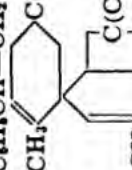
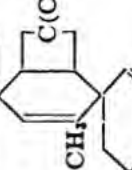
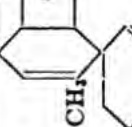
1628. Phytene, $\text{C}_{20}\text{H}_{40}$, to phytane, $\text{C}_{20}\text{H}_{42}$. Liquid phase : platinum-black catalyst. [Willstätter and Mayer, *Ber.*, 1908, **41**, 1475.]

1629. Pentatriacontene to *n*-pentatriacontane. Palladium-black catalyst. [Grün, Ulbrich and Krezil, *Z. angew. Chem.*, 1926, **39**, 421.]

1630. Olefines have been hydrogenated with the Voorhees-Adams platinum oxide catalyst and with the similar palladium oxide catalyst. The platinum catalyst has proved the more efficient: the addition of ferrous salt did not accelerate the reduction of pure olefines. The reduction takes place by 1, 2 addition ($\alpha : \beta$ addition).

1630A. Olefines of the type $\text{CHR} : \text{CH}_2$ are reduced most rapidly, those of the type $\text{CRR}' : \text{CH}_2$ slightly more slowly, further retardation being observed among olefines of the type $\text{CHR} : \text{CHR}'$, depending on the nature of the groups R and R'. β -Methyl- Δ^2 -butylene is reduced much more rapidly than $\alpha\alpha$ -diphenyl- Δ^2 -propylene. Among conjugated olefines, mesityl oxide is much more rapidly reduced than phenyl styryl ketone, while reduction of $\alpha\beta$ -unsaturated acids is generally slow, with a marked absence of regularity. Satisfactory reduction is only obtained with carefully purified materials. The presence of iron retards the reduction of pure products, but may accelerate that of impure materials. Oxygen has no reactivating effect on the catalyst in the reduction of olefines.

TIME REQUIRED FOR THE ABSORPTION OF ONE MOLECULAR EQUIVALENT OF HYDROGEN AT 2 TO 3 ATMOSPHERES PRESSURE

	Substance	Formula	Weight Reduced in G. (0.1 Mole)	Time in Minutes for Absorption of 1 Mol. Equiv. of H ₂ at 2-3 Atmospheres Pressure and 25°			
				PtO ₂ H ₂ O		PdO	
				0.10 G.	0.05 G.	0.10 G.	0.05 G.
1	Eugenol	(CH ₃ O)(HO)C ₆ H ₃ CH ₂ CH=CH ₂	16.4	...	3.5	...	9
2	Safrol	CH ₃ O ₂ C ₆ H ₃ CH ₂ CH=CH ₂	16.2	...	9	...	9
3	Iso-eugenol	(CH ₃ O)(HO)C ₆ H ₃ CH=CHCH ₃	16.4	...	10	...	19
4	Isosafrol	CH ₃ O ₂ C ₆ H ₃ CH=CHCH ₃	16.2	...	11	...	13
5	Anethol	CH ₃ OC ₆ H ₄ CH=CHCH ₃	14.8	...	14	...	8
6	Undecylenic acid	HO ₂ C(CH ₂) ₉ CH=CH ₂	18.4	1.5	2.5	17	32
7	Phenylethylene	C ₆ H ₅ CH=CH ₂	10.4	...	9	...	10
8	Limonene	CH ₃ CH ₂ C(CH ₃)=CH ₂ 	13.6 { 1st bond 2d bond	3	4	42	...
9	Pinene		13.6	6	15	240	...
10	Cyclohexene		8.2	7	...	260	...
11	Trimethylethylene	(CH ₃) ₂ C=CHCH ₃	7.0	3.5	7	13	31
12	Stilbene	C ₆ H ₅ CH=CHC ₆ H ₅ (trans)	18.0	6	12.5	30	135
13	Diphenylethylene	(C ₆ H ₅) ₂ C=CH ₂	18.0	38	...	69	...
14	Diphenylmethylethylene	(C ₆ H ₅) ₂ C=CHCH ₃	19.4	10	21	14	57
15	Mesityl oxide	(CH ₃) ₂ C=CHCOCH ₃	9.8	153	312
16	Benzalacetone	C ₆ H ₅ CH=CHCOCH ₃	14.6	5.5	10	15	43
17	Benzalacetophenone	C ₆ H ₅ CH=CHCOC ₆ H ₅ (trans) (in ethyl acetate)	20.8	11	67	27	87
18	Dimethylacrylic acid	(CH ₃) ₂ C=CHCO ₂ H	10.0	181	...	480	...
19	Maleic acid	HO ₂ CCH=CHCO ₂ H	11.6	7	25	173	...
20	Fumaric acid	HO ₂ CCH=CHCO ₂ H	11.6	18	95	18	120
21	Ethyl maleate	C ₂ H ₅ O ₂ CCH=CHCO ₂ C ₂ H ₅	17.2	10.5 hrs.	...	101	...
22	Ethyl fumarate	C ₂ H ₅ O ₂ CCH=CHCO ₂ C ₂ H ₅	17.2	19.5	41	9	13
23	Cinnamic acid	C ₆ H ₅ CH=CHCO ₂ H(trans)	14.8	31	...	30	...
24	Ethyl cinnamate	C ₆ H ₅ CH=CHCO ₂ C ₂ H ₅ (trans)	17.6	149	...	82	...
25	Sodium cinnamate	C ₆ H ₅ CH=CHCO ₂ Na(trans)	8.5 (0.05 mole)	172	...	26	...
				82	...	52	...

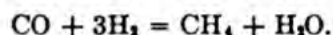
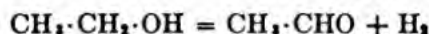
[Kern and Shriner with Adams, J. Am. Chem. Soc., 1925, 47, 1147.]

1631. Laboratory Syntheses of Hydrocarbons. Mailhe⁶ describes some modern laboratory methods for the synthesis of hydrocarbons. Among these are the hydrogenation of carbon monoxide and dioxide with nickel at 250°, and the hydrogenation of olefines and acetylenes with the same catalyst.

ETHERS, ALCOHOLS, ALDEHYDES, ETC.

1632. Hydrogenation of Ethers.⁷ Propyl, isopropyl, butyl, amyl, and isoamyl ethers suffer fission when passed with hydrogen over reduced nickel at 250°–300°. At 180°, phenetole is smoothly converted into cyclo-hexane and ethyl alcohol, whereas at 250° this reaction is accompanied by the production of ethane and phenol. β -Naphthyl methyl and ethyl ethers decompose at 280° in both directions; the aromatic components are further hydrogenated to di- and tetra-hydronaphthalene and tetrahydro- β -naphthol. Guaiacol at 180° under 300 mm. gives the mixed ether $\text{OH} \cdot \text{C}_6\text{H}_{10} \cdot \text{OCH}_3$, together with pyrocatechol and phenol (partly reduced to cyclohexanol). Under similar conditions, diphenyl ether affords dicyclohexyl ether, phenol, cyclohexanol, benzene, and cyclohexane.⁸

1633. Ethyl ether, over nickel at 250°, gives ethane and ethyl alcohol. The alcohol is partially dehydrogenated to acetaldehyde, which, breaking up, gives methane, carbon monoxide, water and hydrogen.



[Sabatier and Senderens, *Bull. Soc. Chim.*, **33**, 1905, 616.]

1634. Allyl ether to propyl ether : gas phase : 138°–140° : nickel catalyst. [Sabatier, *Compt. rend.*, 1907, **144**, 879.]

1635. Allyl alcohol (propenol) to propyl alcohol (and trace of propionic aldehyde). Gas phase : 130°–170° : nickel catalyst. [Sabatier, *Compt. rend.*, 1907, **144**, 879.] Very slow in alcohol solution. [Brochet and Cabaret, *Compt. rend.*, 1914, **159**, 326.] With colloidal platinum gives propyl alcohol. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276.]

1635A. In the vapor phase over an alkaline nickel catalyst at 170°, with hydrogen, propylene oxide yields 35 to 40 per cent of propyl alcohol. The nickel hydrate is washed with 0.1% sodium hydroxide solution before reduction in hydrogen. A similar cobalt catalyst may be used. The reaction is general for the production of primary alcohols from olefine oxides of primary structure. [Canadian Pat. 285,921, Dec. 25, 1928, to Loehr (ass'd to the I. G. Farbenind. A.-G.); *Chem. Abst.*, 1929, **23**, 1136].

1636. *l*- Δ^4 -Pentene- β -ol to *l*-pentane- δ -ol. *l*- Δ^4 -Hexene- β -ol to *l*-*n*-hexane- β -ol. Palladium catalyst. [Levene and Haller, *J. Biol. Chem.*, 1928, **79**, 425, 475.]

1637. The formation of propionaldehyde by passage of allyl alcohol over zinc oxide is, at least in part, due to the reaction of allyl alcohol with acrolein and not to hydrogenation of acrolein nor to intramolecular rearrangement of allyl alcohol.⁹

1638. Methyl-heptenols, hydrogenated under reduced pressure. [Escourrou, *Bull. Soc. Chim.*, Oct., 1928, 1101.]

1639. Ethylmethylheptenol to ethylmethylheptane. Over nickel at 300° C.

1640. Dimethylheptenol to dimethylheptane. Over nickel at 180° C.

⁶ *J. usines gaz.*, 1924, **48**, 34; *Chem. Abst.*, 1924, 1464.

⁷ Marty, *Compt. rend.*, 1928, **87**, 47.

⁸ *Brit. Chem. Abst.*, **1928**, 990A.

⁹ Weston and Adkins, *J. Am. Chem. Soc.*, 1928, **50**, 1930.

1641. By reducing the pressure the removal of the oxygen was avoided and at 14 mm. pressure at 160°–170° C. dimethylheptenol was quantitatively converted into 2, 6-dimethyl-6-heptanol. [Grignard and Escourrou, *Compt. rend.*, 1923, 177, 93; *Chem. Abst.*, 1923, 17, 3478.] This work is summarized in *Bull. Soc. Chim.*, 1928 (iv), 43, 1101, by Escourrou. Cf. Grignard, *Bull. Soc. Chim.*, 1928, 43, 473; *Chem. Abst.*, 1928, 22, 4335.

1642. Dimethyl-allyl-carbinol to dimethyl-propyl-carbinol. Ipatiev's method: "nickel oxide" catalyst. [Sabatier: *Catalysis*, 587.]

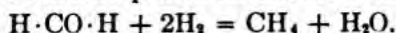
1643. Oleic alcohol to octadecyl alcohol. Liquid phase: platinum-black catalyst. [Sabatier: *Catalysis*, 565.]

1644. The iodohydrin, $\beta\beta$ -diiodomethylpropane- $\alpha\gamma$ -diol (from pentaerythritol) to $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -diol. Pyridine solution: palladized barium sulphate catalyst and magnesia. [Bincer and Hess, *Ber.*, 61B, 1928, 537; *Brit. Chem. Abst.*, 1928, 504A.]

1645. Reduction of Aldehydes and Ketones in the Presence of Platinum-black. Effect of Impurities. The effect of impurities present in the catalyst on the products of the catalytic reduction of aldehydes and ketones with platinum-black was studied by Faillebin by the preparation of a pure platinum catalyst to which known amounts of iron, aluminum, and silica were added. The catalyst was prepared by the method of Loew, impurity being introduced before the reduction of the chloroplatinic acid. In the reduction of aliphatic ketones without a solvent, the use of a pure platinum catalyst favors the reduction of the carbonyl group to a methylene group, the hydrocarbon being the main or sole product. Thus acetone yields propane, methylethylketone yields butane and sec.-butyl alcohol, and methylpropylketone yields pentane. In aqueous solution, acetone also yields only the hydrocarbon when a platinum-silica catalyst is used. In all cases, the use of a platinum-iron catalyst (iron 5–10 per cent) causes almost quantitative reduction to the secondary alcohol, no hydrocarbon being produced. In the reduction of ethyl aceto-acetate, either without solvent or in ether or *n*-hexane solution, a pure platinum catalyst yields only ethyl butyrate, while with a platinum-iron catalyst quantitative reduction to ethyl β -hydroxybutyrate occurs. A platinum-aluminum catalyst gave similar results, only a trace of ethyl butyrate being obtained, but a platinum-silica catalyst yielded both reduction products. In alcoholic solution, however, with a pure platinum catalyst comparable yields of the two reduction products were obtained, this solvent favoring the production of the hydroxymethylene rather than the methylene group. Ethyl β -hydroxybutyrate is not an intermediate in the reduction of ethyl aceto-acetate to ethyl butyrate, since it is not reduced by the platinum catalyst in ether or ethyl acetate solutions. [Faillebin, *Ann. Chim.*, 1925 (x), 4, 156; *Brit. Chem. Abst.*, 1926, 50A.]

1646. Formaldehyde to methanol. In the liquid phase with colloidal osmium catalyst (reduced in and by the formaldehyde solution), at 100° C. the gas evolved contains not only carbon dioxide but also hydrogen, and methane, with minute quantities of carbon monoxide. Experiments show that an increasing evolution of methane is accompanied by a decreasing evolution of hydrogen and that as the ratio, volume of aldehyde solution: weight of osmium, increases, the amount of methane formed decreases, the reaction producing the alcohol always predominating. The time taken for the catalytic action and the gas evolution to reach a maximum is increased by increasing pH and the magnitude of the maximum is reduced. The induction period before the catalytic action begins appears to be the same whether the formaldehyde is heated with the osmium compound or kept cold, and the catalysis differs little whether the osmium is added in the form of the tetroxide, potassium osmate, or potassium chloro-osmate. The volume relations of the gases evolved are about the same in all cases, and when the reaction is concluded the osmium is present in the colloidal condition. The similarity between the present reaction and fermentation by yeast is pointed out.¹⁰

1646A. Formaldehyde to methanol. Gas phase: 90°: nickel catalyst. Simultaneously the formaldehyde is broken up with formation of methane and water,



¹⁰ Müller. *Z. physikal. Chem.*, 1923, 107, 347; *J. Chem. Soc. Abst.*, 1924, i, 833.

Trioxymethylene accumulates on the catalytic surface and stops the reaction. At higher temperatures this surface poisoning is avoided, but the yield becomes progressively poorer, owing to the increasing breakdown to methane. [Sabatier and Senderens, *Compt. Rend.*, 1903, 137, 302.]

Similarly:

1647. Propanal at 102°–145° to propanol. Isobutyric aldehyde at 135°–160° C. to isobutyl alcohol. Amylic aldehyde at 135°–165° C. to ordinary amyl alcohol. Dimethyl propanal to dimethyl propyl alcohol. Dimethyl butyraldehyde to dimethyl butyl alcohol.

1648. Sodium hydrogen sulphite formaldehyde treated with hydrogen at a pressure of 8–10 atmospheres in presence of a nickel catalyst gives sodium formaldehyde sulphonylate. [Feldmann, *Giorn. Chim. Ind. Appl.*, 1925, 7, 406.]

1648A. Aldehyde or ketone sulphonylates are obtained by reducing the corresponding aldehyde or ketone bisulphites or hydrosulphites by means of hydrogen or a gas containing it, at ordinary or increased pressure, with the aid of an activated or unactivated hydrogenation catalyst such as nickel, cobalt, or platinum. In the case of the reduction of formaldehyde bisulphite, the reduction is effected either with an activated hydrogenation catalyst, or at a pressure above 20 atmospheres. The reduction is preferably effected at a low temperature and at a hydrogen-ion concentration about pH7. [Brit. Pat. 308,229, Sept. 19, 1927, to Johnson (from I. G. Farbenind. A.-G.); *Chem. Age* (London), 1929, 411]. Cf., U. S. Pats. 1,714,636 and 7, May 28, 1929, to Schumann and others, ass'd. to Grasselli Dyestuff Corp.; Fr. Pat. 641,509, Sept. 27, 1927, to the I. G.]

1649. Ethanol from Acetaldehyde. The synthesis of ethanol from acetylene may go by way of ethylene or by way of acetaldehyde. Acetaldehyde may be made from acetylene by hydration of the latter. According to Swiss Pat. 74,129, 1916, to the Lonza Company, acetaldehyde mixed with hydrogen (in large excess to dissipate the heat of reaction) and with a trace of oxygen (to inhibit the formation of ether) is passed over a nickel catalyst at 150° C.¹¹ Other catalysts have proved less satisfactory.

1650. Acetaldehyde to ethyl alcohol: 140°; nickel catalyst at 200° destruction of aldehyde. 140° C. is the optimum temperature. The product is almost pure ethanol; there is a little acetal. [Sabatier and Senderens, *Compt. rend.*, 1903, 137, 301.]

1651. Acetaldehyde to carbon monoxide and methane and, partially, resinified: 350°, iron catalyst, Ipatiev's method. [Sabatier: *Catalysis*, 593.]

1652. Preparation of Alcohol by Catalytic Reduction of Acetaldehyde. The most effective nickel catalyst is obtained by soaking pumice with nickel nitrate up to a content of 30 per cent nickel, and heating for six hours at 500° C. in hydrogen passed at a rate of 100 cc. per min. When nickel from nickel nitrate is used, the reduction of the aldehyde is best effected at 140° C., nickel from the oxide is preferably employed at 100° C. The corresponding optimal rates for passing the acetaldehyde are, respectively, 60–70 cc. per min. and 150–170 cc. per min. With a sevenfold excess of hydrogen during reduction a 90 per cent yield of alcohol was obtained. Purified acetaldehyde (97.3–99.3 per cent) was employed. [Nogoshi, *Rep. Osaka. Ind. Res. Lab.*, 1924; *Chem. Abst.*, 1925, 19, 2323.]

1653. Propionic aldehyde to propyl alcohol. Gas phase: 100°–145°: nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1903, 137, 302.]

1654. Butyraldehyde to butyl alcohol with Voorhees-Adams platinum oxide catalyst. For directions see under Benzaldehyde. To avoid acetal formation and to carry the hydrogenation to completion, it is necessary to add 0.3 millimole of sodium hydroxide before the ferrous chloride.

1655. Isobutyric aldehyde, over nickel at 135°–160°, yields 70 per cent isobutyl alcohol and a little acetal (the rest is unchanged aldehyde). [Sabatier and Senderens, *Compt. rend.*, 1903, 137, 302; see under Formaldehyde.]

1656. By Ipatiev's method, with "nickel oxide" catalyst at 250° and 100 atmospheres there is a partial hydrogenation of isobutyric aldehyde to the alcohol. [Ipatiev,

¹¹ Cf. Can. Pat. 134,521.

J. Russ. Phys. Chem. Soc., 1906, **38**, 75, 1907, **39**, 681; *Chem. Abst.*, **1**, 2877; *Ber.*, 1907, **40**, 1270.]

1657. With an iron catalyst, at 350° and 100± atmospheres, the same result was obtained.

1658. Aldol to butane-diol-1, 3 with Voorhees-Adams platinum oxide catalyst. For directions see under Benzaldehyde: 86 per cent yield in two hours. Alcohols are obtained by subjecting to catalytic hydrogenation, in the presence or absence of solvents, the reaction mixture obtained in the condensation of aldehydes or ketones or mixtures of these, e.g., in the aldol condensation. The hydrogenation is effected directly or after removal of the non-condensed aldehydes or ketones, and, when required, after neutralization, but without separation of the condensation products from the condensing agents. Thus from crude aldol is obtained 1:3-butylene-glycol. [Brit. Pat. 309,200, Sept. 28, 1927, to Johnson (from I. G. Farbenind. A.-G.); *Chem. Age* (London), 1929, **20**, 453. See Brit. Pats. 311,671, Feb. 9, 1928, and 311,788, Dec. 2, 1927, to Johnson (from I. G. Farbenind. A.-G.); *Chem. Age* (London), 1929, **20**, 593.]

1659. Isovaleric (isoamyl), aldehyde over nickel at 135°-160°, gives 70 per cent isovaleric alcohol and a little acetal, the rest being unchanged aldehyde.

1660. The same reduction is effected by Ipatiev's method, using a "nickel oxide" catalyst at 250° and 100 atmospheres. [Ipatiev, *J. Russ. Chem. Phys. Soc.*, 1906, **38**, 75.]

1661. With iron tube and iron catalyst, isovaleric acid and amylene are obtained. [Ipatiev, *Ibid.*, 1907, **39**, 681; *Chem. Abst.*, 1907, 2877.]

1662. Heptaldehyde to heptyl alcohol with Voorhees and Adams platinum oxide catalyst. For general directions see under Benzaldehyde. Pressure 2-3 atmospheres: room temperature with rise due to reaction. In the first experiments it was sought to reduce acetal formation by diluting the solvent alcohol. [Carothers with Adams, *J. Am. Chem. Soc.*, 1923, **45**, 1077.] Later it was found better to add 0.3 millimole of sodium ethylate or of sodium hydroxide before adding the ferrous chloride. [Carothers with Adams, *J. Am. Chem. Soc.*, 1924, **46**, 1682.]

1663. Heptaldehyde to heptyl alcohol. Dilute acetic acid solution: colloidal platinum catalyst: 1 atmosphere pressure. [Skita and Meyer, *Ber.*, 1912, **45**, 3589.]

1664. Oenanthaldehyde to heptyl alcohol and some diheptyl ether. Under pressure at 140° C.: Catalyst, mixed oxides of nickel, cobalt and copper. [Ger. Pat. 444,665, Jan. 19, 199, to Riedel.]

1665. γ -Dimethyl- Δ^7 -hexenal and γ -dimethyl- Δ^8 -hexenal (methylisobutylacraldehyde) to β - δ -dimethylhexaldehyde. The two aldehydes, in water solution, are hydrogenated together with a nickel catalyst. [Rupe, Wirz and Lotter. *Helv. Chim. Acta*, 1928, **11**, 965.]

1666. β - γ -dimethyl- Δ^8 -octenaldehyde to β - γ -dimethyloctaldehyde. Similarly are obtained β -methyl- β -tert-butylacraldehyde and γ -dimethyl- β -methylenevaleraldehyde. [Rupe and Giesler, *Helv. Chim. Acta*, 1928, **11**, 656.]

1667. Acrolein (propenal) to propionic aldehyde. Gas phase: 160°: nickel catalyst. The propionic aldehyde is further hydrogenated at 90°-110° more slowly, to propyl alcohol. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 399.]

1668. Preparing Saturated Aldehydes from Unsaturated Aldehydes. Unsaturated aldehydes are treated in the presence of a copper catalyst, with hydrogen insufficient for the complete formation of saturated alcohols; the latter, if formed, are easily separated from the saturated aldehydes. The results are better than those obtained with nickel catalysts. For example, 100 cc. of crotonaldehyde vapor passed over finely divided copper, with 30 liters of hydrogen, at 170°, yield a product containing 80 per cent of butaldehyde and 20 per cent of crotonaldehyde; using 50 liters of hydrogen at 180°, the product contains 60 per cent of butaldehyde and 40 per cent of *n*-butyl alcohol.¹²

1669. Hydrogenating Crotonaldehyde.¹³ The aldehyde is hydrogenated in the

¹² Ger. Pat. 416,906, Mar. 29, 1923, addition. to 350,048 to Badische Co., cf. U. S. Pat. 1,410,223 and Ger. Pat. 407,837; *Brit. Chem. Abst.*, 1926, 108B.

¹³ Holden, Can. Pat. 245,158, Dec. 9, 1924. Impurities are removed from the product by

presence of less water than is necessary to prevent the formation of undesired high-boiling substances during distillation of the reaction product and the necessary amount of water is made up after the hydrogenation and the reaction product is then distilled.

1670. Crotonaldehyde to butyraldehyde. Liquid phase, under 10 to 20 atmospheres hydrogen pressure, at 90°–100° C.: nickel-kieselguhr catalyst. [Brit. Pat. 271,103, May 15, 1926, to Consortium f. electro-chem. Industr. Ges., *Chem. Age* (London), 1927, 17, 86. Cf. Canadian Pat. 276,824, Jan. 3, 1928, to Mugdan and Wimmer; *Chem. Abst.* 1928, 22, 2573.]

1671. Crotonic aldehyde, in the gas phase over nickel, at 125°, yields butyric aldehyde (50 per cent) and butyl alcohol (20 per cent); the alcohol results from the hydrogenation of the aldehyde. [Douris, *Bull. Soc. Chim.*, 1911, (4), 9, 922.] At 170° the proportion of butanol increases.

1672. In absolute ether solution, with platinum-black catalyst, crotonic aldehyde yields butyric aldehyde (70 per cent) and butyl alcohol (30 per cent). [Fournier, *Bull. Soc. Chim.*, 1910 (4), 7, 23.]

1673. Crotonaldehyde to butyraldehyde and butanol. [Carbide and Carbon Chemicals Corp. Brit. Pat. 242,521, Mar. 31, 1925.]

1674. Production of Alcohols from Aldehydes. Aliphatic hydroxyaldehydes or unsaturated aldehydes are treated with hydrogen in the presence of copper catalysts. In starting from simple aliphatic aldehydes, such as acetaldehyde, the copper catalyst is mixed with or deposited upon material capable of promoting condensation of the aldehydes to aldols or to unsaturated aldehydes: *n*-butyl alcohol and ethyl alcohol are obtained from crude aldol and excess hydrogen at 200° C., and *n*-butyl alcohol is derived from crotonaldehyde and hydrogen at 180° C.¹⁴

1674A. The crude condensation product of organic aliphatic compounds, containing at least one carbonyl group, is hydrogenated, preferably at 20–30 atm. and at 50° C., in presence of a catalyst comprising at least one heavy metal from the 1st and 8th groups of the periodic system. The products are mono- and polyhydric alcohols. [Can. Pat. 286,095, Jan. 1, 1929, to Müller and Hoffmann (ass'd to I. G. Farbenind. A.-G.); *Chem. Abst.*, 1929, 23, 1416.]

1675. Methyl-ethyl-acrolein to methyl-pentanol. Ipatiev's method: palladium catalyst: 110 atmospheres: 110°: two or three days. [Sabatier: *Catalysis*, 595.]

1676. α -Methyl- β -ethyl-propenal, in alcohol solution, with colloidal palladium catalyst (gum arabic protective); under 2 atmospheres pressure of hydrogen yields α -methyl-valeric aldehyde and some α -methyl-pentenyl alcohol. [Skita, *Ber.*, 1915, 48, 1486.]

treatment with bromine or chlorine below 60° C., or with hypobromous or hypochlorous acid. The purified alcohol may then be distilled off (Brit. Pat. 312,512, June 20, 1928, to Johnson from I. G. Farbenind. A.-G.; *Chem. Age* (London), 1929, 20, 620).

¹⁴ Ger. Pat. 407,837, Mar. 21, 1922, addition to 350,048 to Badische Co., assignees of Steimmig and Ulrich. *J. S. C. I.*, 1925, 474B.

CHAPTER XVII

HYDROGENATION OF OPEN-CHAIN KETONIC AND ACID COMPOUNDS

KETONIC COMPOUNDS

1700. Acetone. Acetone over a nickel catalyst at 115°–125° C. gives isopropyl alcohol in 85 per cent yield. The yield is less (50 per cent) with a cobalt catalyst. [Sabatier and Senderens, *Compt. rend.*, 1903, **137**, 302.] This reaction, with nickel as catalyst, proceeds very slowly at ordinary pressures. Maxted [*Chem. and Ind.*, 1926, **45**, N. S. 366] distilled acetone in a current of hydrogen, at 100 atmospheres, over granular nickel catalyst. Isopropyl alcohol was rapidly formed. For good yields the hydrogen should be in excess and a circulation method is desirable. The usual commercial method is to agitate acetone, carefully freed from catalyst poisons, with hydrogen under pressure, in presence of a nickel catalyst.

1701. At 200°–300° C. over a nickel catalyst acetone gives methyl-isobutylketone and some diisobutyl-ketone. [Lassieur, *Compt. rend.*, 1913, **156**, 795.]

1702. Ipatiev's method, with copper catalyst, at 280°–300° and 100 to 200 atmospheres, gives a 65 per cent yield of isopropyl alcohol. With iron catalyst at 400° and 103 atmospheres, only 25 per cent isopropyl alcohol was produced in twenty hours. With zinc dust catalyst the yield was 50 per cent.

1703. At 210°–220°, by Ipatiev's method with nickel catalyst, acetone is completely changed to isopropyl alcohol: at 250°–300° decomposition to water, propane and lower saturated hydrocarbons takes place. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 75 and 1907, **39**, 681; *Chem. Abst.*, 1907, **I**, 2877; *Ber.*, 1907, **40**, 1270.]

1704. With nickel suboxide catalyst at 110° and 30 atmospheres pressure, acetone is hydrogenated to isopropyl alcohol. [Senderens and Aboulenc, *Bull. Soc. Chim.*, 1915 (4), **17**, 14.]

1705. Acetone is hydrogenated to isopropyl alcohol, in 50 per cent water solution in presence of platinum-black. [Vavon, *Compt. rend.*, 1912, **155**, 286.]

1706. Acetone to isopropyl alcohol. Liquid phase : 100° C. under 15 atmospheres hydrogen pressure : catalyst mixed carbonates of nickel, cobalt and copper in atomic proportion 60 : 30 : 10. [Ger. Pat. 444,665, Jan. 19, 1919, to Riedel.]

1707. Trifluoro-acetone (trifluorodimethyl-ketone) to trifluoroisopropyl alcohol. [Swarts, *Bull. Acad. Roy. Belg.*, 1927, **13**, V, 175.]

1708. Methyl-ethyl-ketone to secondary butyl alcohol with Voorhees-Adams platinum oxide catalyst. Initial pressure 2.75 atmospheres : ketone 80 g., catalyst 0.5 g. Reaction complete in four hours. [Voorhees with Adams, *J. Am. Chem. Soc.*, 1922, **44**, 1404.]

1709. Methyl-ethyl-ketone to methyl-ethyl-carbinol. 16 per cent water solution : platinum-black catalyst (twelve hours). [Vavon, *Compt. rend.*, 1912, **155**, 286.]

1710. Methyl-isopropyl-ketone to methyl-isopropyl-carbinol. Gas phase : 130°–150° : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1903, **137**, 302.]

1711. Diethyl-ketone to diethyl-carbinol (secondary amyl alcohol). Gas phase : 130°–140° C. : nickel catalyst. Up to 200° no secondary decompositions occur. [Sabatier and Senderens, *Compt. rend.*, 1903, **137**, 302.]

1712. Methyl-propyl-ketone to methyl-propyl-carbinol. Gas phase : 130° – 150° C. : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1903, **137**, 302.]
1713. Pyruvic Acid—Formaldehyde Condensation Product. A lactone, m.p. 140° – 144° C., hydrogenated in presence of platinum-black yields 2 neutral solid isomers, m.p. 219° and 234° – 235° . [Theophilaktov, *J. Russ. Phys. Chem. Soc.*, 1928, **58**, 759.]
1714. Methyl-butyl-ketone to methyl-butyl-carbinol. Gas phase : 150° C. : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1903, **137**, 302.]
1715. Butanone to secondary butyl alcohol. Gas phase : 130° C. : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1903, **137**, 302.] Above 200° secondary decompositions occur.
1716. Butylidene acetone to isobutyl-methyl-ketone. Liquid phase : nickel catalyst : 6 atmospheres hydrogen pressure.
1717. Mesityl oxide under same treatment gave same product. [Grignard and Fluchaire, *Ann. Chim.*, 1928, **9**, 5; *Chem. Abst.*, 1928, **22**, 1951.]
1718. Allyl ketones to saturated ketones. 40 ketone in 200 alcohol : 60° : 10-20g. nickel catalyst. Substrate dissolved in 5 parts of ethyl alcohol. [Cornubert, *Compt. rend.*, 1914, **159**, 78.] Similarly allylcyclohexanone is converted to propyl cyclohexanone.
1719. Acetylacetone to pentanediol-2, 4. Adams' platinum oxide catalyst: 60 per cent yield. [Thayer and McElvain, *J. Am. Chem. Soc.*, 1928, **50**, 3352.]
1720. Butane-dione (diacetyl), $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3$, to butanol-one (2, 3), $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CH}_3$, and butanediol (2, 3), $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$. Gas phase : 140° – 150° : nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 1086.]
1721. γ -Ethyl- Δ^7 -penten- β -one to γ -ethylpentane- β -one. Nickel catalyst. [Cologne, *Bull. Soc. chim.*, 1927, **41** (iv), 325.]
1722. Methyl-hexenone to methyl-hexanone. Gas phase : 160° – 170° : nickel catalyst. [Darzens, *Compt. rend.*, 1905, **40**, 152.]
1723. Dipropyl-ketone to dipropyl-carbinol. Liquid phase, aqueous solution : platinum-black catalyst. [Vavon, *Ann. Chim.*, 1914 (9), **1**, 144.]
1724. Diisopropyl-ketone (isobutyron) to diisopropylcarbinol. Gas phase : below 180° : nickel catalyst. [Amouroux, *Bull. Soc. Chim.*, 1910 (4), **7**, 154.]
1725. 3-Methyl-heptene-(3)-one-(5) to 3-methyl-heptanone-(5) gas phase : 180° : nickel catalyst. [Bodroux and Taboury, *Compt. rend.*, 1909, **149**, 422.] The same reaction, in the liquid phase, is catalyzed by colloidal palladium. [Wallach, *Annalen*, 1904, **336**, 37.]
1726. 4-Methyl-3-octenone to 4-methyl-3-octanone. Nickel catalyst. The unsaturated ketone was prepared by dehydration of an aldol 5-hydroxy-4-methyl-3-octanone. [Powell.]
1727. 2-Methyl-3-octen-6-one to 2-methyl-6-octanone (isohexyl-ethyl ketone). Gas phase : 210° : nickel catalyst. [Thoms and Kahre, *Arch. Pharm.*, 1925, **263**, 241; *Chem. Abst.*, 1925, **19**, 2474.]
1728. 2, 4, 8 Trimethyl-nonene-(4)-one-(6) to 2, 4, 8-trimethyl-nonanone-(6). Gas phase : 280° : nickel catalyst. [Bodroux and Taboury, *Compt. rend.*, 1909, **149**, 422.]
1729. Methyl-nonyl-ketone hydrogenated over nickel at 300° , does not give methyl-nonyl-carbinol, but a mixture of other substances, including a ketone $\text{C}_{22}\text{H}_{44}\text{O}$. [Haller and Lassieur, *Compt. rend.*, 1910, **150**, 1017.]
1730. Pentatriacontanone to pentatriacontane ($\text{C}_{35}\text{H}_{72}$) on hydrogenation. [Grün, Ulbrich and Krczil, *Z. angew. Chem.*, 1926, **39**, 421; *Chem. Abst.*, 1926, **20**, 2818.]
1731. In hydrogenating ketones with nickel catalyst hydrocarbons are produced as well as secondary alcohols. With other metals and with mixtures of metals there is an 80 to 90 per cent yield of wax alcohols. [Grün. Synthesis of waxes. *Z. angew. Chem.*, 1926, **39**, 1037.]
1732. Phorone $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{C}(\text{CH}_3)_2$, to diisobutyl ketone (valerone). Gas phase : 160° – 170° : nickel catalyst. At 225° the alcohol (diisobutyl carbinol) and diisobutane are also formed. [Skita, 1908, *Ber.*, **41**, 2938.]

1733. With colloidal palladium catalyst, phorone is hydrogenated in two stages, first to dihydrophorone and then to diisobutylketone. [Paal, *Ber.*, 1912, **45**, 2221.] Under increased hydrogen pressure (1 atmosphere) this hydrogenation goes to diisobutylcarbinol. [Skita and Ritter, *Ber.*, 1910, **43**, 3393.]

1734. With platinum-black catalyst the degree of hydrogenation seems to vary with the solvent. In ether solution phorone gives diisobutylketone, while in acetic acid solution the hydrogenation goes to diisobutylcarbinol. [Vavon, *Ann. Chim.*, 1914 (9), **1**, 193.]

1735. Homo-isophorones. The mixture of the 4 isomers which results on the treatment of methylethylketone with sodamide at 0° C. when hydrogenated in presence of nickel oxide, by Ipatiev's method, at 220°–240° C. yields the saturated ketone $C_{12}H_{22}O$. With alumina and nickel oxides there results a cyclic hydrocarbon $C_{12}H_{24}$. [Petrov, *Ber.*, 1927, **60B**, 2548; *Brit. Chem. Abst.*, 1928, 156A.]

1736. Homo-isophorone to $C_{12}H_{24}$. Nickel oxide-alumina catalyst (Ipatiev's method) : 260°–280° C. : twenty hours. [Petrov, *Ber.*, 1927, **60**, 2551.]

1737. Acetyl-acetone gives a pentolone, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CO \cdot CH_3$, ethyl alcohol and isopropyl alcohol, intermediate compounds being acetaldehyde and acetone. Gas phase : 150° C. : nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 1086.] Methylacetyl-acetone at 170° C. gave ethanol, butanone and a butanol.

1738. Acetylacetone, by Ipatiev's method, gives pentanediol. Pressure, 116 atmospheres : 109° : palladium catalyst : time, six hours : mechanical stirring desirable. [Ipatiev, *J. Russ. Chem. Soc.*, **44**, 1703.]

1739. Acetylacetone, with platinum-black catalyst gives a glycol, $CH_3 \cdot CHOH \cdot CH_2 \cdot CHOH \cdot CH_3$, with much water and an amyl alcohol, $CH_3 \cdot CHOH \cdot CH_2 \cdot CH_2 \cdot CH_3$. [Vavon, *Compt. rend.*, 1912, **155**, 288.] Acetonyl-acetone to the ether: vapor phase: 190°. [Sabatier and Mailhe, *Compt. rend.* 1907, **144**, 1086.]

1740. Mesityl oxide-oxalic acid ethyl ester (α form) to methylisobutylketone-oxalic acid (ethyl ester). Alcoholic solution : colloidal palladium catalyst. The β form reduces very slowly to the ester of α , α -dimethyltetrahydro- γ -pyrone- α' -carboxylic acid. [Borsche and Thiele, *Ber.*, 1923, **56B**, 2132; *Chem. Abst.*, 1924, **18**, 837.]



1741. Mesityl oxide, $CH_3 \cdot \dot{C} : CH \cdot CO \cdot CH_3$ to 2-methyl-pentanone (4). Gas phase : 160°–170° : nickel catalyst. [Darzens, *Compt. rend.*, 1905, **140**, 152.] The product contains a small quantity of the corresponding alcohol and some isopentane. [Skita, *Ber.*, 1908, **41**, 2938.]

1742. With colloidal palladium working in alcoholic solution, the hydrogenation goes to the 2-methyl-pentanone (4), but in acetic acid solution methyl-iso-butyl-carbinol is formed. [Skita, *Ber.*, 1915, **48**, 1486.] Skita and Ritter obtained the saturated alcohol, also, by working under 5 atmospheres pressure. [*Ber.*, 1910, **43**, 3393.]

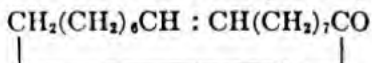
1743. Ipatiev's method, with nickel oxide catalyst, at 140°–150° converts mesityl oxide to methyl-iso-butyl-ketone, with a little of the alcohol. The same result was obtained (in two days) with palladium catalyst at 110°.

1744. Colloidal palladium (gum arabic protective), catalyzes the hydrogenation of mesityl oxide to methyl-iso-butyl-ketone. [Wallach, *Nach. Ges. der Wiss. Göttingen*, 1910, 517; Skita, *Ber.*, 1915, **48**, 1486.]

1745. With colloidal platinum mesityl oxide in aqueous solution is hydrogenated to the ketone, in acetic acid solution, to the alcohol. [Skita, *loc. cit.*]

1746. With platinum-black, first methyl-iso-butyl-ketone, then the alcohol are formed. [Vavon, *Compt. vend.*, 1912, **155**, 287.]

1747. Civetone¹ (odorous constituent of civet) probably,



¹ Civetone contains a 17 C-ring: note that a C_{17} acid has been reported in the analogous secretion of the anal gland of the hyena.

on catalytic hydrogenation by the Paal-Skita method gives a dihydrocivetone. [Ruzicka, *Helv. Chim. Acta*, 1926, **9**, 230.]

1748. Benzyl ethers of sugars : catalytic hydrogenation. See: Freudenberg, Dürr, Hochstetter and others. [*Ber.*, 1928, **61B**, 1735.]

1749. Laevulose (fructose) to α -mannite (*d*-mannitol). Ipatiev's method: the sugar in solution : 130° C. : 100 atmospheres : "nickel oxide" catalyst. Stirring important. The same result is obtained with a palladium catalyst, reduced from the chloride by formate. [Ipatiev, *Chem. Abst.*, 1913, **7**, 1171; *Ber.*, 1912, **45**, 3218.]

1750. Levulose to mannitol. Not less than 3 atmospheres pressure : finely divided metal or metallic oxide catalyst : not above 70° C. [Lupieri and Mayer, French Pat. 468,920, May 6, 1913.] Other methods than the catalytic are given, e.g., electrolytic, nascent hydrogen from formic acid, sodium amalgam produced continuously by electrolysis.

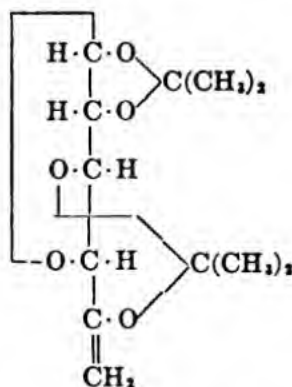
1751. Glucose to sorbitol (sorbite), Ipatiev's method : "nickel oxide" catalyst : 130° at 100 atmospheres. With the palladium catalyst the same result is obtained at 110°. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1002; 1710; *Chem. Abst.*, 1913, **7**, 1171; *Ber.*, 1913, **45**, 3218.] In half-normal potassium hydroxide solution, with platinum-black catalyst, *d*-glucose was slowly reduced to a mixture of *d*-sorbite and *d*-mannite. [Coke, *J. Am. Chem. Soc.*, 1922, **44**, 859.]

1752. Galactose to dulcitol (dulcitol). Ipatiev's method : "nickel oxide" catalyst : 100 atmospheres at 130°.

1753. Triacetyl- β -methyl-*d*-glucoseenide readily absorbs 1 mol. of hydrogen, in acetic acid solution, in presence of spongy platinum. [Helferich and Himmen, *Ber.*, 1928, **61B**, 1825.]

1753A. Compounds such as sugars, starch, cellulose, glycerol, glycosans, glyconic acid and cyclic polyhydroxy compounds are hydrogenated by treatment with activated hydrogen under high pressure (usually 70–100 atmospheres, but possibly ranging from 10 to 100 atmospheres) and at temperatures of above 150° C. (preferably 190–300° C.). Glycerol and its further reduction product, 1, 2-dihydroxypropane, may form the main products. Hydrogenating catalysts are used, such as those of the iron and platinum groups, copper, silver, gold or tungstic acid, which may be mixed with each other and used on a carrier. [Brit. Pat. 299,373, Oct. 24, 1927, to I. G. Farbenind. A.-G.]

1754. Diisopropylidenemethylpentoses are obtained by hydrogenation, in presence of spongy platinum, of an unsaturated compound



This compound is formed by treatment of diisopropylidene-galactose- ξ -iodo-hydrin with sodium methoxide in methanol at 125°–130° C. [Freudenberg and Raschig, *Ber.*, 1929, **62B**, 373; *Brit. Chem. Abst.*, 1929, 427A.]

ACIDS, ETC.

1755. Alkyl esters. In reducing methyl formate or other alkyl esters by hydrogenation a catalyst is used which is prepared by partial reduction of oxides and hydrides of copper (care being taken that no metallic copper is formed) in association with alkaline substances. [U. S. Pat. 1,605,093, Nov. 2, 1926; *Chem. Abst.*, 1927, **21**, 104.]

1756. Acrylic esters to propionic esters. Gas phase: 180° C.: nickel catalyst. [Darzens, *Compt. rend.*, 1907, **144**, 328.]

1757. Similarly ethyl dimethylacrylate to ethyl isovalerate; and other acrylic esters of complicated structure, e.g., normal undecylic acid from undecylenic acid obtained by destructive distillation of castor oil.

1758. Crotonic acid, in gas phase, at 190° , over nickel gives butyric acid quantitatively. [Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909 (8), **16**, 73.] The same result is obtained, in the liquid phase, with colloidal palladium catalyst. [Böeseken, van der Weide and Mom, *Rec. Trav. Chim. Pays Bas.*, 1915, **35**, 260]. Also with colloidal platinum. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276.]

1759. Isocrotonic acid, with colloidal palladium catalyst, is transformed into butyric acid. [Böeseken, van der Weide and Mom, *Rec. Trav. Chim. Pays Bas*, 1915, **35**, 260.]

1760. In general, catalytic hydrogenation of esters of unsaturated acids adds hydrogen at the ethylenic linkages, thus differing from the more drastic action of sodium and other reduction methods. Cf. Darzens, *Bull. Soc. Chim.*, 1907, **4** (1), 179, and contrast Boudeault and Blake's results (using sodium and boiling alcohol), *Compt. rend.*, 1903, **136**, 1676.

1761. Sorbic acid to normal valeric acid. Liquid phase: colloidal platinum catalyst. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276.]

1762. *o*-Hydroxydecanoic acid (methyl ester) to tridecanoic acid (methyl ester). Solution in 90 per cent ethanol: platinum oxide-platinum-black catalyst: 2 to 3 atmospheres. [Noller and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 1074.]

1763. Undecylenic acid (ester) to undecylic acid (ester). Gas phase: 180° : nickel catalyst. [Darzens, *Compt. rend.*, 1907, **144**, 328.]

1764. Oleic Acid to Stearic Acid. Gas phase. At 280° – 300° , vapors of oleic acid carried over a nickel catalyst by a rapid current of hydrogen are transformed into stearic acid. [Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909 (8), **16**, 73.] With a copper catalyst the same hydrogenation can be effected at 300° . Water-gas may, on the large scale, be substituted for hydrogen. [Sabatier, French Pat. 394,957, 1907.]

1765. By Ipatiev's method, using "nickel oxide" catalyst, at 100° and 60 atmospheres, oleic acid is hydrogenated to stearic acid in twelve hours. Prolonged treatment at 25 atmospheres was without effect. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 419 and 855.]

1766. In the liquid phase, at 250° , in presence of nickel catalyst, oleic acid is hydrogenated with a velocity nearly proportional to the pressure of the hydrogen. [Shaw, *J. Soc. Chem. Ind.*, 1914, **33**, 771.]

1767. In the liquid phase, with a colloidal palladium catalyst, oleic acid is 60 per cent hydrogenated to stearic acid in forty-three minutes. [Paal and Gerym, *Ber.*, 1908, **41**, 2273.] Colloidal platinum also catalyzes the transformation of oleic acid to stearic acid. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276.] With palladium-black, oleic acid in ether solution is slowly hydrogenated. The change is accelerated by operating at higher temperatures with the hydrogen under pressure. With a platinum-black catalyst oleic acid is hydrogenated to stearic acid. (Sabatier: *Catalysis*, 565.)

1768. Amyl oleate to amyl stearate. Gas phase: platinized asbestos catalyst. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 419.]

1769. Methyl oleate, methyl erucate, methyl cetoleate and methyl clupanodonate. A study of the velocity of hydrogenation of these esters dissolved in alcohol or in acetic

acid with platinum-black as catalyst. See paras. 3228 to 3242. [Ueno and Kuzei, *J. Soc. Chem. Ind. Japan*, 1927, **30**, 268; *Chem. Abst.*, 1927, **21**, 2458.]

1770. $C_{15}H_{31}O_2$ to stearic acid with platinum-black catalyst. This is an unsaturated acid obtained by treating dibromelaestearic acid with cold potassium hydrate. [Ishio, *J. Pharm. Soc. Japan*, 1923, **501**, 789, through *Chem. Abst.*, 1924, 815.]

1771. Ethyl oleate in ether solution is hydrogenated, in presence of palladium-black, to ethyl stearate. [Sabatier, *Catalysis*, **577**.] At 250° , in presence of nickel catalyst, ethyl oleate is hydrogenated. [Sabatier, *Catalysis*, **601**.]

1772. Elaïdic acid to stearic acid. Gas phase in rapid current of hydrogen: 280° – 300° : nickel or copper catalyst. [Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909 (8), **16**, 73.]

1773. Linoleic acid to stearic acid. Liquid phase: colloidal platinum catalyst. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 276.]

1774. Elaeomargaric Acid. Schrapinger² studied the hydrogenation of Chinese wood oil in order to throw some light on the structure of wood-oil fatty acid. He used the method of Paal³ (palladium-hydrosol as hydrogen carrier), and the modification by A. Skita (higher pressure, for the purpose of accelerating the reaction.) The wood-oil acid to be reduced was dissolved in 30 cc. of alcohol. The palladium chloride was dissolved in 50 cc. of boiling water; 0.5 g. of gum arabic was also separately dissolved in 50 cc. of water. The two solutions were mixed after cooling, and the alcoholic wood-oil acid solution was added; enough ether and alcohol was then added so that a uniform liquid was obtained. Hydrogen, under 1 atmosphere pressure, was then forced into this mixture, and the closed vessel shaken during the process. In two separate experiments, the sodium salt, as well as the free acid, was reduced. It was found that the sodium salt reduces better than the acid itself, owing to the greater solubility of the sodium salt in aqueous alcohol, thus eliminating the possibility of coating the colloidal palladium particles by precipitated acid. After the reaction was finished, the solution was raised to boiling, then filtered and finally evaporated. The residue was dissolved in hot water, and acidulated with hydrochloric acid. The precipitated acid was recrystallized from alcohol, possessed a melting-point of 69° to 69.5° C. and showed the following composition:

1. 0.2138 g. substance gave:

0.5969 g. CO_2 corresponding to 0.1627 g. C.,

0.2386 g. H_2O corresponding to 0.0266 g. H.

2. 0.1941 g. substance gave:

0.5424 g. CO_2 corresponding to 0.1479 g. C.,

0.2135 g. H_2O corresponding to 0.0238 g. H.

Calculated for $C_{18}H_{36}O_2$ C = 75.98 per cent, H = 12.76 per cent,

Found C = 76.09 per cent, H = 12.44 per cent,

C = 76.19 per cent, H = 12.26 per cent.

The product obtained, therefore, was stearic acid, whereby it was proved that elaeomargaric acid is an acid with a simple (straight) chain. Yield: 63 per cent of the theory.

1775. Selective hydrogenation of alpha-elaestearic acid (from tung oil). See: [Böeseken, *Rec. Trav. Chim.*, 1927, **46**, 619; full abstract, *Brit. Chem. Abst.*, 1927, 1169; and Böeseken and van Krimpen, *Proc. K. Akad. Wetensch.*, Amsterdam, 1928, **31**, 238; *Brit. Chem. Abst.*, 1928, 736A.]

1775A. Hydrogenation of polymerized alpha-elaestearic acid (from Chinese wood oil) yielded chiefly stearic acid. [Bauer, *Chem. Umschau Fette, Oele, Wachse u. Harze*, 1926, **33**, 53; *Chem. Abst.*, 1926, **20**, 3585.]

² Dissertation, Karlsruhe, 1912; Stevens and Armitage, *China Wood Oil*, Vol. II, Part 2, 2770.

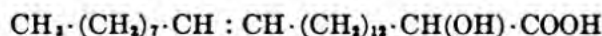
³ *Ber.*, 1905, **38**, 1406, 2414; 1907, **40**, 2209; 1908, **41**, 2273, 2282.

1776. Castor oil (ricinoleic acid glycerides) by partial hydrogenation to glycerides of λ -hydroxystearic acid : Nickel : 80° C. [Grün and Czerny, *Ber.*, 1926, **59**, 54.]

1777. Walden. Optical inactivity of hydrogenated ricinoleic acid and its derivatives. [*Chem. Umschau Fette Oele Wachse Harle*, 1925, **32**, 275.]

1778. 12-Hydroxystearic acid is prepared from castor oil by limited hydrogenation, avoiding attack of the hydroxyl group. Oil 5 kg., 1.5 per cent nickel on a carrier, hydrogenation at barely 80° for three hours until about three-quarters saturated. The product is "alcoholized" with acid alcohol (2 per cent HCl) giving the mixed esters. From the ethylester a mixture of *cis*- and *trans*- $\Delta^{12,13}$ -octadecenic acid can be obtained by the catalytic action of β -naphthalene sulphonic acid, β -C₁₀H₇SO₃H. [Grün and Czerny, *Ber.*, 1926, **59B**, 54.]

1779. Unsaturated Hydroxy-acid of Cerebrosides. An acid, probably



is present in cerebroside fractions and on catalytic hydrogenation takes up 2 atoms of hydrogen, giving cerebronic acid. Cerebronic acid is probably C₂₁H₄₀O₃ and not C₂₅H₄₀O₃. [Klenk, *Z. Physiol. Chem.*, 1928, **174**, 214.]

1780. Protolichestearic acid, C₁₉H₃₂O₄, from *Cetraria islandica*, with hydrogen and platinum-black gives a dihydro-derivative C₁₉H₃₄O₄.

Lichestearic acid (derived from the above by heating with acetic anhydride) gives, on heating in a vacuum, a lactone which with hydrogen and palladinized barium sulphate yields a dihydro-derivative. [Asahina and Asano, *J. Pharm. Soc. Japan*, 1927, No. **539**, 1.]

1781. α -Elemic acid to a dihydro-acid : ethanol solution : palladinized kieselguhr catalyst. [Bauer, *Ber.*, 1928, **61B**, 343.]

1782. Nervonic acid, C₂₄H₄₆O₂, to *n*-tetracosic acid C₂₄H₄₈O₂; colloidal palladium. [Klenk, *Z. Physiol. Chem.*, 1926, **157**, 283, 291.]

1783. Reduction of Polybasic α -Hydroxy-acids under the Influence of the Combined Action of Catalysts.* The action of hydrogen under pressure on heated solutions of sodium malate, tartrate, and citrate in the presence of aluminum oxide and nickel oxide is characterized by reduction of the hydroxyl group by hydrogen with production of the corresponding saturated polybasic acid and decomposition of the molecule into monobasic acids. The first change is observed only with malic and tartaric acids, which give succinic acid in 50 per cent yield and very small amount respectively. Decomposition of the acids affords formic and acetic acids, carbon dioxide, and methane. Methylsuccinic acid is obtained from citric acid in rather more than 30 per cent yield.*

1784. The sodium salts of α -hydroxy- α' -methylsuccinic, α -hydroxy- $\alpha\alpha'$ -dimethylsuccinic and α -hydroxy- α -methyl- α' -ethylsuccinic acids (at 250° C., 60–68 atmospheres hydrogen pressure, with nickel-alumina catalyst) underwent the same reduction of the hydroxyl. Yields of 25–30 per cent methyl succinic acid, of 18–45 per cent formic and acetic acids and traces of higher fatty acids were obtained. In the case of α -hydroxy- α -methyl- α' -ethylsuccinic acid, 30 per cent of butyric acid was formed. [Razubaiev, *J. Russ. Chem. Phys. Soc.*, 1927, **59**, 1071.]

1785. Maleic Anhydride to Succinic Anhydride.* Maleic anhydride vapor is passed with hydrogen over a catalyst (nickel at 180° C., copper at 300° C.) other than platinum; or the anhydride is reduced with hydrogen in ethyl acetate in presence of a nickel catalyst at 15° C.

1786. Fumaric acid to succinic acid. Aqueous solution of sodium salt : colloidal palladium catalyst. [Paal and Gerum, *Ber.*, 1908, **41**, 2273–2277.]

* Ipatiev and Razubaiev, *Ber.*, 1927, **60B**, 1973 (1927).

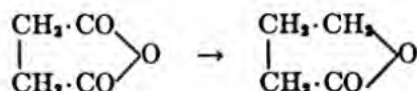
* *Brit. Chem. Abst.*, **1927**, 1054A.

* I. G. Farbenind. A.-G., Assignees of F. Webel, Ger. Pat. 441,002, Dec. 18, 1924. *Brit. Chem. Abst.*, 1927, 924B.

1787. Succinic anhydride to propionaldehyde.⁷

1788. Carboxylic acids or their anhydrides are acted on by reducing gases such as hydrogen, coal gas, producer gas, or water-gas at high temperatures, in presence of hydrogenation catalysts such as chromium, iron, copper, manganese, cobalt and their oxides. As promoters may be used lead, beryllium, cerium, uranium, zinc and their oxides.⁸

1789. Succinic anhydride to butyro-lactone. Gas phase : low temperature : nickel catalyst.



[Eijkmann, *Chem. Weekblad.*, 1907, 4, 191.]

1790. Muconic acids (methyl esters) to adipic acid (methyl ester). Palladium catalyst. [Farmer and Duffin, *J. Chem. Soc.*, 1927, 402.]

1791. Citraconic acid and itaconic acid to pyrotartaric acid. Liquid phase : colloidal platinum catalyst. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 276. Cf. Asahina et al., *Acta Phytochemica*, 1924, 2, 1.]

1792. Dihydrochaulmoogric and dihydrohydnicarpic acid homologs. [See Hiers and Adams, *J. Am. Chem. Soc.*, 1926, 48, 1089.]

1793. Laevulinic acid, γ -ketovaleric acid, over nickel at 250°, gives the hydroxy-acid. This, being a γ -hydroxy acid, loses water at the temperature of the reaction, and forms γ -valerolactone. [Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909 (8), 16, 78.]

1794. Ethyl β -methyl- Δ^{α} -tridecene- α -dicarboxylate to ethyl β -methyltridecane- α -dicarboxylate. Platinum-black catalyst. [Ruzicka and Stoll, *Helv. Chim. Acta*, 1927, 10, 680. An investigation of muscone.]

1795. Aconitic acid with colloidal platinum hydrogenates to the saturated tricarballic acid. [Fokin, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 276.]

1796. Dilactone ($\text{C}_{10}\text{H}_{12}\text{O}_6$) from condensation of 2 molecules of α -keto- β -methylol-butyrolactone on hydrogenation with platinum sponge yields 2 isomers : $\text{C}_{20}\text{H}_{20}\text{O}_{12}$. [Feofilaktov, *Ber.*, 1927, 59B, 2765; *Chem. Abst.*, 1927, 21, 896.]

1797. The dilactone $\text{C}_{22}\text{H}_{24}\text{O}_8$ formed by oxidation of dianhydrostrophanthidin, yielded a tetrahydro derivative on hydrogenation in presence of palladium. This was further hydrogenated, with difficulty, to a hexahydrodilactone $\text{C}_{22}\text{H}_{28}\text{O}_8$. [Jacobs and Collins, *J. Biol. Chem.*, 1925, 65, 491.]

1798. Methyl Esters of the ω -Hydroxy Aliphatic Acids. The methyl esters of the ω -aldehydo acids were reduced to the corresponding methyl esters of the ω -hydroxy acids according to the method of Carothers and Adams for the reduction of aldehydes to primary alcohols. A solution of 0.2 mole of the aldehyde ester in 100 cc. of 95 per cent ethyl alcohol, to which had been added 0.2 g. of platinum oxide catalyst and 2 cc. of freshly prepared 0.1 m. ferrous sulphate solution, was shaken with hydrogen under about 2.5–3 atmospheres pressure. Usually about two hours were required for the absorption of the theoretical quantity of hydrogen.⁹

1799. *d*-Gluconic acid to *d*-glucose. Aqueous solution : 10–17 pounds hydrogen pressure : platinum oxide catalyst : 14–28 per cent yields. Galactonic acid gave 30–45 per cent yields of dulcitol. Mannonic acid gave yields of 2 per cent or less. [Glanfeld and Shaver, *J. Am. Chem. Soc.*, 1927, 49, 2305; *Chem. Abst.*, 1927, 21, 3353.]

⁷ This is given as an example of the method disclosed in Brit. Pat. 290,319, Jan. 7, 1927, to I. G. Farbenind. A.-G. (Another example is the production of benzaldehyde from phthalic anhydride.)

⁸ *Chem. Abst.*, 1929, 23, 850.

⁹ Lyan and Adams, *J. Am. Chem. Soc.*, 1929, 51, 627.

CHAPTER XVIII

NON-NUCLEAR HYDROGENATION OF CARBOCYCLIC COMPOUNDS*

PENTA-CYCLIC COMPOUNDS

1800. Cyclopentanone. In 15 per cent solution in ether, with a platinum-black catalyst, cyclopentanone can be hydrogenated to cyclopentanol. [Vavon, *Compt. rend.*, 1912, **155**, 287.] Yohe and Adams [*J. Am. Chem. Soc.*, 1928, **50**, 1505] using the Adams' catalyst, worked with 95 per cent ethanol as solvent. With 100 cc. of the solvent to 1 mole of the ketone, when reduction of the platinum oxide had taken place in presence of the latter, considerable reduction to cyclopentane and water occurred.

1801. Methyl (1) cyclopentanone (3) to methylcyclopentane. Gas phase : 250° : nickel catalyst. [Zelinsky, *Ber.*, 1911, **44**, 2781.] At 150° the α and β -methyl-cyclopentanones, however, are hydrogenated to the corresponding alcohols, but there also occurs a union of the two rings, with the formation of large quantities of dimethyl-cyclopentyl-pentanones. [Godchot and Taboury, *Bull. Soc. Chim.*, 1913 (4), **13**, 591.]

1802. Isopropylidene-cyclopentanone to isopropyl-cyclopentanone. Liquid phase : colloidal palladium catalyst. [Wallack, *Annalen*, 1912, **394**, 362.]

1803. Ketodihydrodicyclopentadiene on catalytic hydrogenation gives ketotetrahydrodicyclopentadiene. [Wieland, Bergel, Schwarz, Schepp and Fukelmann, *Annalen*, 1925, **446**, 13.]

1804. The hydroxymethylene derivative of 1 : 2 : 2 : 3-tetramethylcyclopentyl-methyl-ketone, $C_8H_{17} \cdot CO \cdot CH : CH \cdot OH$, hydrogenated with nickel catalyst gives 1 : 2 : 2 : 3-tetramethylcyclopentyl- β -hydroxyethylketone. [Rupe and Perret, *Helv. Chim. Acta*, 1926, **9**, 97.]

SIX-MEMBERED CARBOCYCLIC RING COMPOUNDS

HYDROCARBONS

1805. Cresyl-propenes (2), ortho-, meta-, and para, in the gas phase, with nickel catalyst, not very active, or specially treated so as not to catalyze the hydrogenation of the benzene ring, at 160°-180°, or above 300° with active nickel, are converted into the corresponding cymenes. [Sabatier and Murat, *Compt. rend.*, 1913, **156**, 184.]

1806. 1-Phenyl-2-propyl-pentene to 1-phenyl-2-propyl-pentane. Gas phase : 300° : nickel. [Murat and Amouroux, *J. Pharm. Chim.*, 1912, (7), **5**, 473.]

1807. $\alpha\alpha$ -Diphenylethylene (stilbene) to $\alpha\alpha$ -diphenylethane (dibenzyl). Gas phase : 220°-240° C. : nickel, moderately active catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915 (9), **4**, 284-297.]

1808. 1,3-Diphenylpropene, ω -Benzyl-styrol, $C_6H_5 \cdot CH_2 \cdot CH : CH \cdot C_6H_5$, to 1,3-diphenylpropane, $CH_2(CH_2C_6H_5)_2$. Alcohol solution : palladium-calcium carbonate catalyst. [Stoermer and Thier, *Ber.*, 1925, **58**, 2607.]

1809. Diphenyl-butenes to diphenyl-butanes. Gas phase : 200° : nickel catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915, (9), **4**, 284-297.]

1810. Diphenyl-pentenenes (diphenyl-1,3-ethyl-2-propenes) to diphenyl-pentanes. Gas phase : 225° : nickel catalyst of moderate activity. [Sabatier and Murat, *Ann. Chim.*, 1915 (9), **4**, 297.]

* For reasons special to each case some hydrogenations wholly or partially nuclear are treated in this chapter and in Chapter XIX.

1811. 9 : 12-Diphenyl- Δ^9 : 11 -diphensuccindadiene to 9 : 12-diphenyl- Δ^{10} -diphensuccindane. Aqueous solution : palladium catalyst. 9 : 12-Diphenyldiphensuccindane and other analogous compounds are also dealt with in the original paper. [Brand and Muhl, *J. prakt. Chem.*, 1925, **110** (ii), 1.]

1812. 9 : 12-Di-*n*-propyl-diphensuccindadiene-9 : 11 to 9 : 12-di-*n*-propyl-diphensuccindane. Alcoholic solution : palladium-charcoal catalyst. [Brand and Sasaki, *Ber.*, 1925, **58**, 2548.]

1813. 9 : 12-Di-*n*-propylidene-diphensuccindane to 9 : 12-di-*n*-propyl-diphensuccindane (*Ibid.*). 9 : 12-Di-*iso*-propyldiphensuccindadiene 9-11 to 9 : 12-di-*iso*-propyldiphensuccindane (*Ibid.*).

1814. $\alpha\zeta$ -Diphenylbutadiene to $\alpha\zeta$ -diphenyl-*n*-hexane. Platinum oxide or palladium oxide catalyst. [Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 87-151.]

1815. Diphenylpolyenes: catalytic hydrogenation. See: Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 87; *Chem. Abst.*, 1928, **22**, 1769.

1816. Hydrogenation of Hydrocarbons Resulting from Decomposition of Alkali-metal Organic Compounds.¹ $C_{22}H_{22}$ (obtained by the action of lithium on diphenyl dichlorethylene or on diphenyldibromomethylene) to $C_{22}H_{24}$. Palladium-barium sulphate catalyst. A liquid dihydrophenanthrene (resulting from the action of ethanol on lithium-phenanthrene) gave 2 tetrahydrophenanthrenes. The 1, 2-dihydro derivative of 1, 2, 4, 5-tetraphenyl benzene gave tetraphenyl benzene on treatment with hydrogen in presence of palladium.

1817. Benzene and Toluene from Technical Xylene and from Solvent Naphtha. A process which is not, strictly, a hydrogenation but a demethylation by means of hydrogen in presence of metallic sulphides and alumina is described by Juchnovski (Yukhnovskii) in *Ukraine. Chem. J.*, 1928, **4** (Tech.), 65; good abstracts will be found in *Chem. Abst.*, 1929, **23**, 377, and in *Brit. Chem. Abst.*, 1928, 844B.

1818. Purification of Crude Benzole by Selective Hydrogenation.² Crude benzol is purified and desulphurized by heating at high temperature and pressure in presence of a catalyst immune from sulphur poisoning and of hydrogen or hydrogenating gases. For example crude benzol containing thiophene may be passed in a current of hydrogen over a contact mass composed of molybdic acid and zinc oxide pressed together. The product will be free from thiophene and unsaturated compounds. Pressures should be above 50 atmospheres, temperature, 450° C. (842° F.). Molybdenum, tungsten, or chromium may serve for the contact mass.

HYDROXYL COMPOUNDS

1819. Phenols to hydrocarbons. High pressure (70-80 kg.-cm.²) : 480° C. : alumina catalyst, also thoria and silica. Phenol gives mainly benzene; the cresols mainly toluene; cyclohexanol a mixture of hydrocarbons, only slightly unsaturated.³

1820. Hydrogenation of Organic Substances at High Temperature and Pressure Using Non-hydrogenating Catalysts.⁴ Complex organic substances, when heated with

¹ Addition of alkali metal at carbon-carbon linkages. Schlench and Bergmann (with 17 others). *Ann.*, 1928, **463**, 1; *Chem. Abst.*, 1928, **22**, 4493.

² *Brit. Pat.* 258,576 (convention date Sept. 15, 1925) to I. G. Farbenind. A.-G.

³ Kling and Florentin, *Compt. rend.*, 1927, **184**, 885. Cf. *Idem, Ibid.*, 1926, **182**, 526, and *Idem, Bull. Soc. chim.*, 1927, **41**, (iv), 1314. Cf. *Brit. Pats.* 276,007 (next paragraph) and 279,488 (Oct. 23, 1926) to Florentin, Kling and Matignon. According to the later patent, with complex material such as low temperature tars, a second catalyst may be employed (e.g., a halide of magnesium, zinc, iron, chromium or aluminum), and the hydrogenation effected in two stages at different temperatures. *Chem. Abst.*, 1928, **22**, 2835. *Brit. Pat.* 276,007, May 26, 1926, describes the obtaining of light hydrocarbons from animal and vegetable oil by treating the oil in the continuous liquid phase at 350°-480° with hydrogen at a pressure of at least 45 kg./cm.² in the presence of a dehydrating catalyst, e.g., thoria, alumina, clay, or silica. *Brit. Chem. Abst.*, 1927, 836B.

⁴ Kling and Florentin, *Compt. rend.*, 1926, **182**, 526-527.

hydrogen under pressure, are more readily reduced in the presence of a catalyst such as aluminum chloride, which causes the intermediate formation of substances less stable than the original. Thus, cyclohexanol, heated at 420°–440° C. with hydrogen under pressure, in presence of aluminum chloride, gives an excellent yield of cyclohexane and some normal hexane. Naphthalene under similar conditions yields chiefly benzene, toluene, xylenes, etc. The method is of general application.⁶

1821. Cracking and Hydrogenating Oxygen-containing Organic Compounds. Florentin, Kling and Matignon⁶ treat organic compounds containing hydroxyl or carboxyl groups with hydrogen (with or without carbon monoxide or hydrocarbon gases) at 350°–480° C. and under a pressure not less than 45 kg. per square centimeter, in presence of dehydrating catalysts (e.g., thoria, alumina, clay, silica). Saturated light oils are produced. Among the raw materials mentioned are: phenol, cresols, phenolic oils, cyclohexanol derivatives, shale oil, fatty oils. An instance is mentioned where shale oil yielded 80 per cent of saturated oil of sp. gr. 0.855, 48 per cent boiling below 205° C.

1822. Reduction of Phenols to Aromatic Hydrocarbons. A process which does not seem to employ a catalyst is described for the reduction of phenols by Borrmann.⁷ Phenolic compounds, such as low-temperature tar phenols, are treated with hydrogen in vertical coils contained in a furnace into which hot gases are admitted from the top. The phenols are preheated and vaporized in the lower portion of the coils, and, after admixture with hydrogen, are reduced during their passage through the upper portion of the coils. The issuing gases are fractionated and condensed, the uncondensed portion being absorbed in oil scrubbers. The heating gases are charged into the furnace at a temperature of 800°–900°, and the mixture of phenol vapor and hydrogen is maintained at 750°.⁸

1823. Production of Benzene by Reaction between Phenolic Vapors and a Reducing Gas. In the reduction of phenol to benzene at 750° by hydrogen or gases containing it, efficient temperature control is obtained by separately heating the phenol vapors and the reducing gases to the reaction temperature before mixing. Each component is heated by passing part of the gas or vapor through a superheater in which it is raised above the reaction temperature, by-passing the remainder, and mixing the superheated part with the remainder as required to obtain the necessary temperature.⁹

1824. Hydrogenation of Phenols in Presence of Ferrous Oxide. Ramage treats phenols such as crude "tar acids," with hydrogen in presence of ferrous oxide at 700° C. and obtains toluene and benzene.¹⁰

1825. Hydrogenation of Low-temperature Tar Phenols.¹¹ Low-temperature tar phenols or tar oils containing them are distilled with steam at high temperatures over substances which decompose steam with the liberation of hydrogen, e.g., iron or coke. Benzene and its derivatives are obtained. By regulation of the temperature some control may be had over the nature of the products. High temperatures yield low-boiling benzole. A good yield of phenol itself is obtained by incomplete decomposition. Using low-temperature tar phenols and distilling with steam at 650° C., a yield of 60–65 per cent of hydrocarbons is obtained; phenols, chiefly phenol, amount to 7 per cent.

1826. Phenols to Hydrocarbons by a Bergin Type Process. The phenol or mixture of phenols is heated at 470° with hydrogen under 90 atmospheres pressure for one hour. To obtain the maximum reduction the light oils and water formed should be removed continuously from the autoclave. The process yields 80 per cent of light hydrocarbons

⁶ *Brit. Chem. Abst.*, 1026, 381A.

⁷ *Brit. Pat.* 263,082, Dec. 17, 1925; *Chem. Age* (London), Feb. 19, 1927, 190.

⁸ *Ger. Pat.* 403,192, June 6, 1922.

⁹ *J.S.C.I.*, 1925, 347B.

¹⁰ *Brit. Pat.* 273,493, July 7, 1927 to Irinyi.

¹¹ *U. S. Pat.* 1,430,585, Oct. 3, 1922; *C. A.*, 1922, 16, 3903.

¹² *Ger. Pat.* 422,035, July 16, 1921 to Oberschlesische Kokswerke & Chem. Fabr. A.-G. and Supan.

distilling to 250°. Methane and water are formed as by-products. The unchanged phenol can be again submitted to the process.¹²

1827. The interior of metal apparatus for the manufacture of hydrocarbons from phenols is coated with a substance capable of hindering carbon deposit, e.g., a layer of metal sulphide, formed by passing sulphur-containing gases through the apparatus before use.¹³

1828. Phenol to benzene. Vapor phase at 750° C. The vapor and the reducing gas are separately preheated.¹⁴ Regulation of the heat is secured by the admission of cold gas; this is necessary for the production of phenol.¹⁵ See para. 1823.

1829. Cresols to Toluene. Stadnikov, Gavrilov and Vinogradov¹⁶ reduced cresols by treatment with a catalyst composed of iron on which is deposited activated charcoal. The mechanism is that the cresol is reduced, the carbon is oxidized; next a portion of the cresol is decomposed and a fresh deposit of active carbon forms on the iron and so on. Paracresol gives the best results. The maximum yield possible is 92.5 per cent; 90 per cent is realized with pure cresol.

1830. ω -Trifluoro-*m*-cresol to ω -trifluoromethylcyclohexanol and ω -trifluoromethylcyclohexane. Platinum-black catalyst. [Swarts, *Bull. Soc. Chim. Belg.*, 1923, **32**, 367.] This, however, it should be noted, is a nuclear hydrogenation.

1831. Phenyl-ethyl alcohol (phenylmethyl carbinol) to ethyl-benzene. Gas phase : 380° C. : nickel catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915, (9), **4**, 257.]

1832. Cyclohexane-diol (1, 2) ether to cyclohexanol. Gas phase : 160° : nickel catalyst. Yield quantitative. [Brunel, *Ann. Chim. Phys.*, 1905 (8), **6**, 237.]

1833. Benzyl alcohol to toluene. Gas phase : 370° : nickel catalyst : 80 per cent yield. [Sabatier and Murat, *Ann. Chim.*, 1915 (9), **4**, 258.] At lower temperatures, some methyl cyclohexane is formed. With excess of methanol vapor, over thoria, at 420°, toluene is also produced.

1834. By Ipatiev's method, with an iron catalyst, at 350° and 96 atmospheres benzyl alcohol yields toluene and dibenzyl. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 489; *Chem. Centr.*, 1908 (2), 1098.]

1835. Anethol, $p\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$, to methoxy-propyl-benzene; by Ipatiev's method : 95° : 50 atmospheres : nickel catalyst (10 per cent) : in four hours. At 200° : twenty hours : gives propyl-cyclohexane, water and methane.

1836. At low and moderate pressures, without solvent, with 10 per cent nickel at 60°–80°, *p*-methoxy-propyl-benzene is produced : rapidly at 15 atmospheres; five times slower at atmospheric pressure. [Brochet and Bauer, *Bull. Soc. Chim.*, 1915 (4), **17**, 50; *Cf. Compt. rend.*, 1914, **159**, 326 and 190.]

1837. Hydroquinone at 250° over nickel forms first phenol, then benzene. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 429.] But at 130° the product is cyclohexadiol (1, 4) or quinone, *cis*-form, while at 160° the product is a mixture of the *cis*- and the *trans*-forms with some phenol and cyclohexanol. [Sabatier and Mailhe, *Compt. rend.*, 1908, **146**, 1193.]

1838. Quinone is also produced when hydroquinone is hydrogenated by Ipatiev's method, with "nickel oxide" catalyst at 200°. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 75; *Chem. Centr.*, 1906 (2), 86; *Ber.*, 1907, **40**, 1281.]

1839. Pyrocatechol or pyrocatechin ortho-dioxybenzene, benzene-diol (1, 2) to cyclohexadiol (1, 2), (m.p. 75°). Gas phase : 130° : nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1908, **146**, 1193.] Above 250° phenol is first produced, then benzene. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 429.]

1840. Tannins and Related Substances. Passage from the Flavone to the Catechin

¹² French Pat. 618,520, July 6, 1926; Ger. Pat., date Dec. 2, 1925; *J.S.C.I. Suppl.*, Feb. 17, 1928, 118.

¹³ Ger. Pat., 431,479, June 21, 1922, to Fischer; *Brit. Chem. Abst.*, **1926**, 865B.

¹⁴ Brit. Pat. 273,493, July 8, 1926, to Irinyi; *Chem. Abst.*, 1928, **22**, 1982.

¹⁵ *Chem. Age* (London), 1927, **17**, 152.

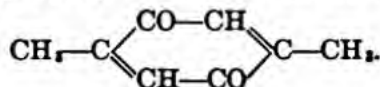
¹⁶ *J. Chem. Ind.* (Russia), 1926, **2**, 228; *Chem. Abst.*, 1926, **20**, 1064, and 1926, **20**, 2841.

Series. Catalytic reduction of quercetin pentamethyl ether (3 : 5 : 7 : 3' : 4'-penta-methoxyflavone) in presence of platinum-black affords 11 per cent of *dl*-epicatechin pentamethyl ether. Luteolin tetramethyl ether (5 : 7 : 3' : 4'-tetramethoxyflavone), m.p. 192°, obtained by simultaneous hydrolysis and methylation of luteolin tetra-acetate, is hydrogenated under similar conditions, yielding 24 per cent of deoxyepicatechin tetramethyl ether (*Ibid.*, 419), identified as the monobromo-derivative, m.p. 155–156°. [Freudenberg and Kammüller, *Annalen*, 1927, 451, 209; *Brit. Chem. Abst.*, 1927, 251A.]

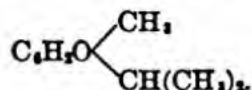
1841. Attempts to isolate intermediate products of hydrogenation of cyanidin chloride were unsuccessful. When, however, tetramethyl-luteo-linidin chloride is treated with 1 mol. of hydrogen in 96 per cent alcoholic solution in presence of platinum-black and a little hydrochloric acid, α -3 : 4-dimethoxybenzoyl- β -2'-hydroxy-4' : 6'-dimethoxy-phenylethane is obtained. In absolute alcohol, ring-fission does not occur, the final and only isolable product being deoxyepicatechin tetramethyl ether (*cf.* preceding para.). 2 : 4 : 6-trimethoxybenzaldehyde is reduced by hydrogen and platinum-black to methylphloroglucinol trimethyl ether, b.p. 100°–105°/1 mm., m.p. 27°–28°. When a nickel catalyst is used, a good yield of 2 : 4 : 6-trimethoxybenzyl alcohol, m.p. 63°, is obtained. [Freudenberg and Harder, *Annalen*, 1927, 451, 213; *Brit. Chem. Abst.*, 1927, 251.]

1842. Quinone to hydroquinone. Gas phase : 190° C. : nickel catalyst. Quantitative yield. At 220° to 250° phenol, water and the hydrocarbon are formed. [Sabatier and Mailhe, *Compt. rend.*, 1908, 146, 457.]

1843. Toluquinone to tolyhydroquinone at 200° C. over nickel. Paraxyloquinone to



Thymoquinone [*Ibid.*] to



1844. Phenylcrotyl ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$, to phenyl-*n*-butyl ether. [Claisen and Tietze, *Ber.*, 1926, 59B, 2344.]

1845. Benzohydrol (diphenyl-carbinol), $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{OH}$, to diphenyl-methane. Gas phase : 380° C. : nickel catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915, (9), 4, 259.]

1846. Phenyl-*p*-cresyl carbinol to phenyl-*p*-cresyl-methane. Gas phase : 350°–380° : nickel catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915 (9), 4, 259.]

1847. *s*-Distyrylethylene glycol to α β -diphenylhexatriene. Platinum-black catalyst. [Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, 11, 87–151.]

1848. Triphenyl carbinol to triphenyl-methane. Gas phase : 400° : nickel catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915 (9), 4, 258.]

1849. Hydrogenated di[hydr]oxy-diphenylmethane Compounds. Hydrogenated *pp*-dihydroxydiphenylmethane derivatives, of general formula $(\text{HO}\cdot\text{C}_6\text{H}_4)_2(\text{HO}\cdot\text{C}_6\text{H}_4)\text{CRR}'$ and $(\text{HO}\cdot\text{C}_6\text{H}_5)_2\text{CRR}'$, in which R and R' are either the same or different aryl or alkyl groups, are obtained by the action of hydrogen in the presence of a catalyst on condensation products of a ketone with a phenol. Thus *pp*'-dihydroxydiphenyldimethylmethane ($\beta\beta$ -4 : 4'-dihydroxydiphenylpropane), from acetone and phenol, on hydrogenation at 170°–180° and 10–15 atmospheres with a nickel catalyst (5 parts) yields β -*p*-hydroxy-phenyl- β -4-hydroxycyclohexylpropane, b.p. 213°/0.8 mm. In the presence of colloidal palladium at 50° complete saturation yields a mixture of bis- β -4-hydroxycyclohexylpropanes, b.p. 102°–106°/12 mm., having an odor of lily of the valley and probably consisting of a mixture of *cis*, *cis-trans*, and *trans-trans* isomerides. At 150°–170° in the presence of nickel bis- $[\beta$ -6-hydroxy-*m*-tolyl] propane similarly yields β -6-hydroxy-*m*-tolyl- β -4-hydroxy-3-methylcyclohexylpropane, b.p. 218°/0.8 mm., when

the reaction is stopped after 6 atoms have been absorbed, and on complete saturation a mixture of stereoisomeric bis- $[\beta$ -3-methyl-4-hydroxycyclohexyl]propanes, b.p. 108°–112°/12 mm., having an odor of hyacinths. The condensation product of phenol and methyl ethyl ketone similarly yields a mixture of stereoisomeric bis- $[\beta$ -4-hydroxycyclohexyl]butanes, b.p. 120°–125°/14 mm.¹⁷

1850. Condensation products of phenols with ketones are treated with hydrogen under pressure in presence of a catalyst. E.g., the condensation product of α -naphthol and acetone gives 4-isopropyl-1-naphthol.¹⁸

1851. Dehydrooxybinaphthalene oxide to binaphthol and oxybinaphthalene oxide. In ether or in hexahydrotoluol: light excluded: Platinum sponge. [Pummerer and Rieche, *Ber.*, 1926, **59B**, 2161.]

1852. A resinous distillate is obtained from the condensation products of *ar*-tetrahydro- β -naphthol and cyclohexanol. Catalytic hydrogenation of the condensation products also gives a resin. [Alberti, *Annalen*, 1926, **450**, 304.]

BASIC COMPOUNDS INCLUDING AMINO-ACIDS

1853. Amines of the Hydroaromatic Aliphatic Series.¹⁹ In making amines containing hydroaromatic and aliphatic radicles and a hydroxyl group in at least one aliphatic radicle, it is laid down that, when compounds containing aldehyde or ketone groups are used in the condensation, reduction is necessary to obtain the corresponding hydroxyl group. Thus the reaction product of cyclohexanone and ethanolamine is reduced with hydrogen in presence of a nickel catalyst. Similar substances are produced by the action of hydroxyaldehydes and hydroxyketones, such as aldol or sugars, on hydroaromatic amines, followed by hydrogenation.

1854. Monomethylenearyl amines (or polymerization products) to monomethylaryl amines. Palladized carbon: alcoholic solution: room temperature. [Merck Chem. Fabr., assignees of Maeder and Krauss, Ger. Pat. 437,975, 1924.]

1855. Phenacylalkylamine (salts) to carbinols. Ten per cent nickel on pumice or asbestos. Phenacylmethylamine (hydrobromide) gives β -methylamino- α -phenyl-ethyl alcohol. β -amino- α -phenylethyl alcohol and β -methylamino- α -phenyl-propyl alcohol are similarly obtained.²⁰

1856. Methyl [3, 4, 5-trimethoxybenzylidene] amine to the benzylamine. Colloidal palladium catalyst. Sonn (with others), *Ber.*, 1925, **58B**, 1103.

1857. Secondary Amines from Cyclic Ketones and Amino Alcohols. Cyclohexyldi-(β -hydroxyethyl) amine is obtained by hydrogenation of a mixture of cyclohexanone and alcoholic β -aminoethyl alcohol with nickel at 130°–140° C. and 35 atmospheres hydrogen pressure. Similar products are obtained from homologous cyclic ketones and aminoalcohols (other methods are described). The products are insecticides and germicides and their acyl derivatives are plasticizers.²¹

1858. Cinnamalcyclohexylamine catalytically reduced gives 3-phenylpropylcyclohexylamine.

1859. 1-Ethylimino-2-benzalpropionic acid gives 3-phenyl-1-*N*-ethylaminobutyric acid.

1860. Cinnamaethylamine gives phenylpropyl ethylamine.

1861. 3-phenyl-1-*N*-cyclohexylaminobutyric acid gives 3-cyclohexyl-1-*N*-cyclohexylaminobutyric acid.

¹⁷ Brit. Pat. 252,594, Nov. 9, 1925, to Chem. Fabr. auf Aktien (vorm. E. Schering) and H. Jordan. Cf. para. **2150**. These hydrogenations are nuclear. *Brit. Chem. Abst.*, 1926, 720B. Cf. Brit. Pat. (application) 309,865, Apr. 16, 1928 to same.

¹⁸ Can. Pat. 281,114, June 19, 1928, to Jordan, Schoeller and Clerc, assigned to Chem. Fabr. auf Aktien (vorm. E. Schering).

¹⁹ Brit. Pat. 297,484, May 23, 1927, to Johnson (from I. G. Farbenind. A.-G.).

²⁰ Brit. Pat. 280,574, Nov. 10, 1927, to Merck; *Brit. Chem. Abst.*, 1929, 149B.

²¹ Brit. Pat. 297,484, May 23, 1927, to Johnson as agent of I. G. Farbenind. A.-G.

1862. 1-Amylimino-2-benzalpropionic acid gives 3-phenyl-1-*N*-amylaminobutyric acid.

1863. 1-Ethylimino-2-anisalpropionic acid gives 3-anisyl-1-*N*-ethylaminobutyric acid.

1864. 1-Amylimino-2-piperonalpropionic acid gives 3-piperonyl-1-*N*-amylaminobutyric acid.

1865. Amylimino-2-cinnamalpropionic acid gives first 5-phenyl-1-*N*-amylaminopentancarboxylic acid and, on further reduction, the pentanecarboxylic acid. [Skita and Wulff, *Ann.*, 1927, **455**, 17; *Chem. Abst.*, 1927, **21**, 2882.]

1866. Malachite green to leuco-malachite green. In solution: nickel catalyst. [Brochet, *Compt. rend.*, 1915, **160**, 306.]

1867. Methylstyryl carbamate to methyl beta-phenyl-ethylcarbamate. Nickel catalyst (aluminum is inactive). [Rinkes, *Rec. trav. chim.*, 1927, **46**, 268.]

1868. **Syntheses of Amino-Acids.**²² The condensation product, of benzylidenecyclohexylamine and pyruvic acid is hydrogenated, in presence of colloidal platinum, to a cyclohexylaminophenylpropanecarboxylic acid, $C_{18}H_{27}O_2N$. Similarly, isobutylidenecyclohexylamine, gives with pyruvic acid an unstable compound, which is hydrogenated to a cyclohexylaminoheptanecarboxylic acid. Ethylidenecyclohexylamine and pyruvic acid, however, in dry ethereal solution yield acetaldehyde and the extremely unstable, yellow, amorphous α -cyclohexyliminopropionic acid, which is readily hydrogenated to α -cyclohexylaminopropionic acid. A second, less unstable, condensation product, α -cyclohexylamino- α -hydroxypropionic acid, prepared from cyclohexylamine or α -propylidenecyclohexylamine, and pyruvic acid in ethereal solution, yields the same cyclohexylalanine on reduction. The constitution of the latter is confirmed by synthesis from cyclohexylamine and α -bromopropionic acid, and also by conversion into cyclohexylethylamine. Contrary to the statements of Knoop and Oesterlin, faintly acid aqueous-alcoholic solutions containing ethylamine and pyruvic or glyoxylic acid are hydrogenated, in presence of colloidal platinum, to α -ethylaminopropionic acid, and ethylaminoacetic acid, respectively. In this reaction, the ethylamine may be replaced by aldehyde-ammonia, which is reduced to ethylamine under these conditions, or by ethylidene-ethylamine. Under analogous conditions, alanine (30 per cent) is obtained from a solution containing ammonia and pyruvic acid. A new synthesis of β -aminoacids is afforded by the observation that, unlike the parent substance, the acetyl and *N*-alkyl derivatives of ethyl β -iminobutyrate are readily hydrogenated. Accordingly, the following derivatives of ethyl butyrate: β -acetimido-; β -cyclohexylimino-; β -ethylimino-; β -isoamylimino-; and β -phenylimino-, were reduced to the ethyl esters, respectively, of β -acetamido-, β -cyclohexylamino-, β -ethylamino-, β -isoamylamino-, and β -anilino- butyric acids.²³

1869. Benzoylaminocinnamic acid to benzoyl-phenylalanine. Platinum-black catalyst; 25 per cent: slight plus pressure of hydrogen: eight days. [Waser, *Helv. Chim. Acta*, 1925, **8**, 117.]

1870. Vanillidene hippuric acid hydrogenated in absolute alcohol, at room temperature and at 70°, with platinum-black catalyst gave only 10 per cent of an ethylbenzoic acid. [Waser, *Helv. Chim. Acta*, 1925, **8**, 117.]

1871. Methyl-3-methyl-4-benzylidenehydantoin-1-acetate (2 isomers) to methyl-3-methyl-4-benzylhydantoin-1-acetate. Palladium catalyst. [Hahn and Evans, *J. Am. Chem. Soc.*, 1928, **50**, 806.]

1872. **Peptides.** α -Acetamidocinnamoyl-*D*-glutamic acid yields a mixture of *n*-acetyl-*L*-phenylalanyl-*D*-glutamic acid and *n*-acetyl-*D*-phenylalanyl-*D*-glutamic acid. Palladium black catalyst. [Bergmann, Sterne and Witte, *Annalen*, 1926, **449**, 277-302.]

1873. **Arginine Dipeptides: Syntheses.**²⁴ 2-Acetaminocinnamoyl-*D*-arginine, hydrogenated with palladium, gives *N*-acetylphenyl-alanyl-*D*-arginine.

²² Skita and Wulff, *Ann.*, 1927, **453**, 190.

²³ *Brit. Chem. Abst.*, 1928, 559A.

²⁴ Bergmann and Koster, *Z. Physiol. Chem.*, 1927, **167**, 91; *Chem. Abst.*, 1927, **21**, 2876.

1874. Carbimides: Oxidiazines. Catalytic reduction of 2-methylimino-4-keto-3 : 5-dimethyl-6-ethylidene-1 : 3 : 5-oxdiazine yields 2-methylimino-4-keto-3 : 5-dimethyl-6-ethyl-1 : 3 : 5-oxdiazine. [Slotta and Tschesche, *Ber.*, 1927, **60B**, 1011.]

1875. Aromatic Bases : Non-catalytic Hydrogenation.²⁵ Isocyclic or heterocyclic aromatic bases are hydrogenated by treatment with alkali metals or alkaline-earth metals and alcohols in presence of an indifferent solvent. [*J.S.C.I.*, 1918, **37**, 487A.]

ACIDS

1876. Carboxylic acids to aldehydes. Vapor phase: activated hydrogenation catalyst: gas containing carbon monoxide : 200°-250° C. *Examples:* Benzoic acid to benzaldehyde, iron catalyst, or catalyst made by reducing intimate mixture of chromium and iron oxides, or containing cerium, chromium and iron. For producing acetaldehyde a cobalt-iron catalyst may be used.²⁶

1877. Cinnamic Acid. Formic acid, in the presence of spongy or colloidal palladium, decomposes with the evolution of hydrogen, this nascent hydrogen converts cinnamic to phenyl-acetic acid.²⁷

1878. In solution in twice its weight of amyl alcohol, in presence of 10 per cent of nickel, at 100° and 15 atmospheres pressure, cinnamic acid is completely changed to phenylpropionic acid in forty-five minutes. Sodium cinnamate, dissolved in four parts of water, can be hydrogenated this way in the cold. [Brochet and Bauer, *Bull. Soc. Chim.*, 1915 (4), **17**, 50, and *Compt. rend.*, 1914, **159**, 190.]

1879. But by Ipatiev's method, using his nickel catalyst at 300° under 100 atmospheres, sodium cinnamate gives sodium cyclohexyl-propionate. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1414.] Under the same conditions, but with the copper catalyst, the aromatic nucleus is not hydrogenated and the product is the phenylpropionate. [Ipatiev, *loc. cit.*]

1880. With ruthenium-black catalyst 0.05 g. to 0.5 g. cinnamic acid in 2 cc. glacial acetic acid, phenylpropionic acid is formed in eight hours. Rhodium-black is more active and in the conditions just described converts cinnamic acid into phenylpropionic acid in three hours. [Madinaveitia, *Soc. Espan. Fis. Quím.*, 1913, **11**, 328.]

1881. Methyl cinnamate to methyl phenylpropionate. Solution in methanol : 15 atmospheres : room temperature : nickel catalyst : three hours. [Brocher and Bauer, *Bull. Soc. Chim.*, 1915 (4), **17**, 50 and *Compt. rend.*, 1914, **159**, 190.]

1882. Ethyl cinnamate to ethyl-phenyl-propionate. 50 per cent solution in ethyl alcohol : 70° : nickel catalyst : 7 hours. [Brochet and Cabaret, *Compt. rend.*, 1914, **159**, 326.] On the analogy of methyl cinnamate, the reaction should be much accelerated at 15 atmospheres pressure. At atmospheric pressure it is very slow.

1882A. Ethyl β -*p*-tolyl-cinnamate to ethyl β -phenyl- β -*p*-tolylpropionate. Nickel catalyst: autoclave. [v. Braun, Manz and Reinsch, *Ann.*, 1929, **468**, 277.]

1883. Phenyl-isocrotonic acid (ethyl ester) to ethyl-phenyl-butyric acid (ethyl ester). Gas phase : 180° : nickel catalyst. [Darzens, *Compt. rend.*, 1907, **144**, 328.]

1884. Piperonyl-acrylic acid to piperonyl-propionic acid. Liquid phase : room temperature : nickel catalyst : 15 atmospheres. [Brochet and Bauer, *Bull. Soc. Chim.*, 1915 (4), **17**, 50.]

1885. γ -*p*-Tolyl- Δ^{β} -pentenoic acid to γ -*p*-tolyl-valeric acid. Nickel catalyst. [Rupe and Schütz, *Helv. Chim. Acta*, 1926, **9**, 992.]

1886. α -Oxy- β -diphenylene-acrylic acid methyl ester to α -oxy- β -diphenylene-propionic acid methyl ester. Absolute ethanol solution: Adams' platinum-black catalyst: 1.588 g. ester to 45 mg. platinum oxide. [Kuhn and Levy, *Ber.*, 1928, **61B**, 2244.]

²⁵ Ger. Pat. 305,347, Oct. 5, 1915, to the Bayer Co.

²⁶ Brit. Pat., 267,925, to I. G. Farbenind. A.-G., convention date March 19, 1926.

²⁷ Verein. Chininfabr., Zimmer & Co., Ger. Pat. 267,306, 1914, *Chem. Centr.*, 1915 (1) 88.

1887. *d*-Pimaric Acid: Hydrogenation of Two Double Bonds. Although physical constants of *d*-pimaric acid (a resin acid $C_{30}H_{50}O_2$) had led to the conclusion that it possessed two double linkages, no tetrahydro derivatives had resulted from the application of the usual reducing methods. It was therefore held that one of these double bonds was more resistant to saturation than the other.

1888. Ruzicka, Huyser and Seidel²⁸ have recently succeeded in preparing tetrahydro derivatives by catalytic hydrogenation:

1. *d*-Pimaric acid 5 g., without solvent, was hydrogenated in a rotating autoclave, under a hydrogen pressure of 42–48 atmospheres, for three days. The product was a stereoisomeric mixture of *dihydro* isomerides, m.p. 200°–203° C.

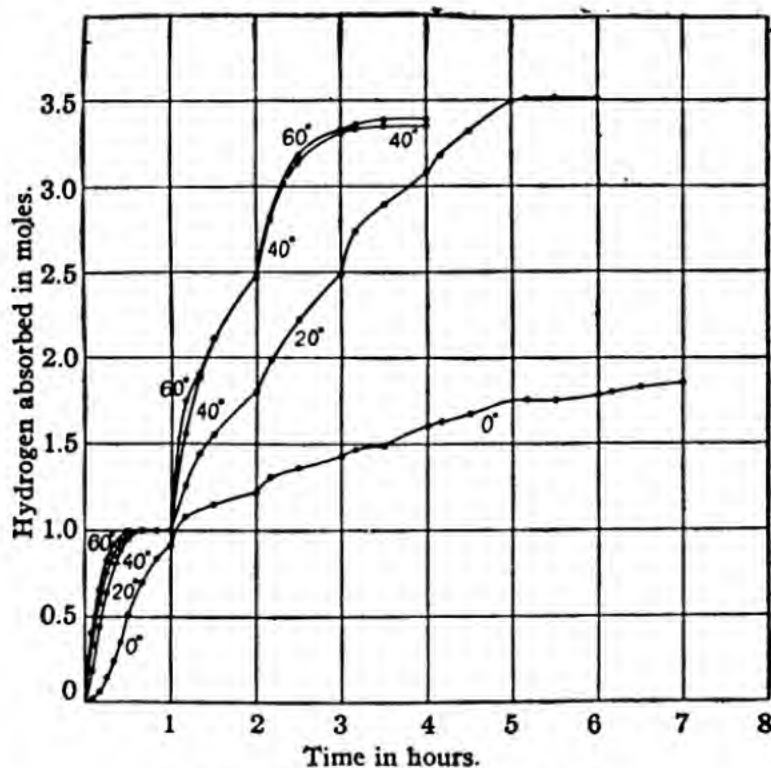


FIG. 25c.—SEE ALSO FIG. 25b, PAGE 183.

Reduction of 0.1 mole of furfural (Cf. Chap. XXVII, page 282) 0.244 g. of catalyst, 1 cc. of *M*/10 ferrous sulfate.

The catalyst becomes active and the absorption of hydrogen becomes rapid much more quickly in the higher temperature than in the lower temperature reductions. $PtO_2 \cdot H_2O$ is brown and the active catalyst is black, so the change in color from brown to black is an indication of the formation of the active catalyst. The platinum black which has been used as a catalyst for the reduction of furfural is not a catalyst for the reduction of furyl alcohol, and the only way it can be made to add more hydrogen to the latter compound is to change its surface by activation. Pierce and Parks. (*J. Am. Chem. Soc.* 1929, **51**, 3384.)

2. *d*-Pimaric acid 2.5 g., in ethyl acetate solution, hydrogenated, with Adams' platinum oxide catalyst 0.2 g., gave also a mixture of dihydro acids, m.p. 238°–239° C. the fraction with the lowest melting point melted at 228°–229° C.

3. *d*-Pimaric acid 3 g. in acetic acid with 1.0 g. of the Adams' catalyst, hydrogenated for fifteen hours at 50° C. gave a mixture of tetrahydro acids, $C_{30}H_{54}O_2$. One of these acids, purified, had m.p. 238°–239° C.

²⁸ *Rec. trav. chim.*, 1928, **47**, 363.

1889. The evidence that this was due to an addition of hydrogen at two bonds is: (1) the elementary composition; (2) the measurement of the hydrogen absorbed; (3) the crystallographic unity of the purified acid m.p. 238°–239° C., which was different in optical characteristics from the acid m.p. 238°–239° C. obtained in Exp. 2; (4) *d*-Pimaric acid is resistant to even strong acids; therefore the tetrahydro derivatives did not result from an opening of a ring by action of the acid used.

1890. The existence of two double bonds is confirmed by the action of perbenzoic acid: *d*-pimaric acid takes up 1 atom of oxygen quickly and a second atom slowly: the dihydro acid takes up 1 oxygen atom, the tetrahydro acid none.

1891. α -Benzoxyl- β -benzal propionic acid (acetate) to α -benzoxyl- γ -phenyl-butyric acid (acetate). Alcohol solution: palladinized barium sulphate catalyst. [Stoermer and Schenck, *Ber.*, 1928, **61B**, 2319.]

1891A. Desylidene cyanoacetic acid (ethyl and methyl esters) to α -cyano- β -benzoyl- β -phenylpropionic acid (esters). Alcohol solution: palladized barium sulphate catalyst. [Bachér, *J. pr. Chem.*, 1929, [ii], **120**, 301.]

1891B. Lactone of δ -hydroxy- $\beta\delta$ -diphenyl- Δ^7 -pentenoic acid in acetone solution in presence of palladized charcoal takes up 2 mols of hydrogen yielding $\beta\delta$ -diphenyl-*n*-valeric acid. [Mannich and Butz, *Ber.*, 1929, **62B**, 461.]

1892. Dicarboxylic acids to aldehydes. Vapor phase, 250°–400° C.: iron, chromium, copper, manganese, cobalt (metals or oxides): hydrogen or carbon monoxide as reducing gas. Examples: phthalic anhydride to benzaldehyde; succinic anhydride to propylaldehyde; the succinic anhydride may be obtained by prior hydrogenation of maleic anhydride at 180° C.²⁰

1893. Polybasic Alpha-hydroxy and Keto Acids, with nickel oxide—alumina catalysts, by Ipatiev's method, condensation, reduction and decomposition. [Ipatiev and Razuvaev, *Ber.*, **60B**, 1927, 1971, 1980; *Chem. Abst.*, 1928, **22**, 386.]

1894. Benzoylphenylcyclopropane carboxylic acid (sodium salt) hydrogenated in presence of palladinized barium sulphate undergoes a ring-splitting, yielding the sodium salt of α -phenacylhydrocinnamic acid. [Stoermer and Schenck, *Ber.*, 1928, **61B**, 2318.]

1895. Ethyl cinnamoylpyruvate to ethyl β -phenylpropionylpyruvate. [Borsche and Peter, *Ann.*, 1927, **453**, 148.]

1896. Mandelic Acids: hydrogenation.²⁰ When benzyl benzoate is reduced in boiling xylene solution by hydrogen and palladium, toluene and benzoic acid are produced. The esters of other alcohols do not similarly give the corresponding hydrocarbon, at least only those which can be regarded as substituted benzyl alcohols in containing an α -phenyl group. Acetylmandelic acid, i.e., α -carboxybenzyl acetate, is similarly smoothly reduced to acetic acid and phenylacetic acid (yield 20 per cent in boiling xylene, 60 per cent in boiling tetralin). *p*-Methoxy- and *o*-chloro-phenylacetic acids are likewise obtained from the acetates of the corresponding mandelic acids. The diacetyl derivative of *o*-hydroxymandelic acid gives directly *o*-hydroxyphenylacetic acid, the *o*-acetyl group being simultaneously removed, in the form of acetaldehyde. The method affords a ready means of obtaining substituted phenylacetic acids.²¹

²⁰ Brit. Pat. 290,319, Jan. 1, 1927, to Johnson, from the I. G.; *Brit. Chem. Abst.*, 1928, 515B.

²⁰ Rosenmund and Schindler, *Arch. Pharm.*, 1928, **266**, 281.

²¹ *Brit. Chem. Abst.*, 1928, 1005A.

CHAPTER XIX

NON-NUCLEAR HYDROGENATION OF CARBOCYCLIC COMPOUNDS

ALDEHYDES

1900. Catalytic Reduction of Aromatic Aldehydes. Hydrogenation of benzaldehyde, anisaldehyde, and *o*-chlorobenzaldehyde in glacial acetic acid solution in the presence of palladized barium sulphate with one molecular proportion of hydrogen yields a mixture of approximately equal parts of unchanged aldehyde, corresponding alcohol, and hydrocarbon, since aldehyde and alcohol are reduced at nearly equal rates. Addition of quinoline diminishes the velocity of the second action to such an extent that the alcohols can be obtained in 62 to 75 per cent yield. In the cases of piperonal and vanillin, the rates of the two reactions are sufficiently different to allow the preparation of either alcohol or hydrocarbon by the use of one or two molecular proportions of hydrogen; addition of quinoline is unnecessary. [Rosenmund and Jordan, *Ber.*, 1925, 58B, 160; *J. Chem. Soc.*, 1925, *Abst.*, i, 257.]

1901. Hydrogenation of Aldehydes and Ketones in Presence of Platinum-black. Failliebin¹ extended his studies of the hydrogenations of aldehydes, etc., with pure platinum-black and with the same catalyst plus iron, aluminum or silica (*cf.* para. 1645) to aromatic compounds. The differential effect is most marked in the case of ketones. For details the original article should be consulted.

1902. Benzaldehyde to benzyl alcohol with Voorhees and Adams' platinum-oxide catalyst. Benzaldehyde 21.2 g., ethyl alcohol (95 per cent strength) 50 cc., platinum oxide catalyst 0.1725 g., 0.2 *M* ferrous chloride solution 0.5 cc. : 3 atmospheres total pressure : twenty-five minutes for total conversion. With less solvent the reaction is slower; with 100 cc. it goes a little quicker. Other solvents tried gave different reaction velocities in the following order : acetone, glacial acetic acid, ethyl acetate, petroleum ether, absolute ethyl ether, pyridine, benzene. This is the decreasing order of velocities. With methyl alcohol there is formation of acetal (dimethyl acetal of benzaldehyde), except when the solvent has been distilled over sodium. It is necessary to keep the hydrogen-ion concentration as low as possible, to prevent acetal formation. Free alkali causes precipitation of iron hydroxide. With absolute ethyl alcohol as solvent the hydrogenation goes further, with a slow formation of toluene.

1903. Benzaldehyde to benzyl alcohol. Liquid phase: colloidal palladium catalyst. Hydrogenation is difficult and incomplete. [Skita and Ritter, 1910, *Ber.*, 43, 3393.] With colloidal platinum, in addition to benzyl alcohol, toluene and methyl-cyclohexane are formed. [Skita, *Ber.*, 1915, 48, 1486.] With platinum-black in alcohol solution the yield of benzyl alcohol is almost quantitative. With 10 g. of platinum-black a gram molecule of benzaldehyde can be hydrogenated in a few hours. [Vavon, *Compt. rend.*, 1912, 154, 359.] See graphs by Carothers and Adams; Figure 25a, page 172.

1904. Benzaldehyde to benzyl alcohol. Liquid phase: 130°–170° C., 25 atmospheres hydrogen pressure : catalyst composed of mixed carbonates of nickel, cobalt and copper in atomic proportions [*sic*], 60 : 30 : 10. At 210°–220° C. cyclohexyl-methylcarbinol is obtained in good yield without formation of benzhydrol.²

¹ *Ann. Chim.*, 1925, 4 (X), 410; *Brit. Chem. Abst.*, 1926, 50A.

² *Ger. Pat.* 444,665, Jan. 19, 1919, to Riedel, addition to 369,374.

1905. Catalytic hydrogenation of products other than fatty compounds is effected with the aid of a non-precious catalyzing metal, such as nickel, with or without a support, by causing hydrogen to react by frequently renewing the surfaces between the gas and the catalyzing metal (in the form of an impalpable powder impregnated with the material to be hydrogenated), while maintaining the mixture at a moderate temperature and under a moderate pressure. The substance to be treated may be a liquid, a molten solid, a solution, or a suspension. The process is applicable to the production of benzyl alcohol from benzaldehyde; methylphenyl carbinol from acetophenone; *p*-phenylenediamine and *p*-aminophenol from *p*-nitroaniline and *p*-nitrophenol, respectively; cyclohexanol from phenol, and the production of reduction products of nitrosated and nitro compounds generally. [*Chem. Abst.*, 9, 355 (1915). Cf. *Chem. Abst.*, 8, 2780.]¹

1906. Benzaldehyde to various hydrocarbons. Gas phase : nickel catalyst : 210° to 235° gives: toluene and benzene:



At the same time the aldehyde is partly decomposed with benzene and carbon monoxide:



The carbon is partially reduced to methane. Other side reactions produce a certain amount of methylcyclohexane and cyclohexane. [Sabatier and Senderens, *Compt. rend.*, 1903, 137, 301.]

1907. Benzaldehyde vapor passed over thoria at 420°, with excess of methanol vapor yields toluene. [Sabatier and Murat, *Compt. rend.*, 1913, 157, 1499; *Bull. Soc. Chim.*, 1914 (4), 15, 227.]

1908. By Ipatiev's method, with an iron catalyst, at 280° and ± 100 atmospheres, benzaldehyde gives a mixture of toluene and dibenzyl. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 489; *Chem. Centr.*, 1908 (2), 1098.] By the same method, with a "nickel oxide" catalyst, benzaldehyde at 200° gives toluene and methyl-cyclohexane; at 280°, toluene, dibenzyl and resinous products. [Ipatiev, *Ber.*, 1908, 993-1001; *J. Russ. Phys. Chem. Soc.*, 1906, 38, 75 *Chem. Centr.*, 1906 (2), 86.]

1909. Benzaldehyde-halogen derivatives. With Voorhees and Adams platinum oxide catalyst. For general directions see under Benzaldehyde.

p-Chlorobenzaldehyde to *p*-chlorobenzyl alcohol.

p-Bromobenzaldehyde to *p*-bromobenzyl alcohol.

o-Chlorobenzaldehyde to *o*-chlorobenzyl alcohol.

The solvent in each case is 95 per cent ethyl alcohol. No acetal is formed and no considerable amount of free halogen acid.

1910. Cinnamic aldehyde, dissolved in 20 parts of alcohol, is converted into phenylpropionic aldehyde by Paal's method (colloidal palladium catalyst). [Paal and Gerum, *Ber.*, 1908, 41, 2273 and 2277.] The same result is obtained with colloidal platinum. [Skita, *Ber.*, 1915, 48, 1685.]

1911. On the other hand, with platinum-black (method of Willstätter), the product is phenylpropyl alcohol. [Vavon, *Compt. rend.*, 1912, 154, 359.]

1912. Cinnamic aldehyde hydrogenated with the Voorhees-Adams' platinum oxide catalyst, cannot be completely reduced unless the catalyst is frequently reactivated by aëration. If an appropriate amount of iron salt is present and the operation is stopped when 1 molecular equivalent of hydrogen has been absorbed, the product is almost pure cinnamyl alcohol. With certain proportions of zinc and iron salts the reduction goes to phenylpropyl alcohol without the necessity for aëration. With other proportions (see below) of zinc and iron salts the hydrogenation automatically stops at the

¹ Brit. Pat. to Brochet, 16,936, July 23, 1913. See also Brochet, Brit. Pat. 22,523, 1913, addition to 16,936, 1913.

cinnamyl alcohol stage. Various experimental conditions were investigated and are tabulated in the original paper. The optimum conditions seem to be: 0-1 mole of aldehyde; 100 cc. ethyl alcohol (95 per cent); 0.2 g. catalyst; 0.2 millimole ferrous chloride; 0.03 millimole zinc acetate : pressure, 2 to 3 atmospheres. [Tuley, with Adams, *J. Am. Chem. Soc.*, 1925, **47**, 3061.]

1913. Phenylacetaldehyde to phenylethyl alcohol. Liquid phase : 1 to 5 atmospheres pressure : colloidal palladium catalyst. [Skita and Ritter, *Ber.*, 1910, **43**, 3393.] With colloidal palladium catalyst phenylacetaldehyde is also hydrogenated to phenylethyl alcohol, accompanied by some ethylbenzene, cyclohexanol, cyclohexanone and cyclohexane. [Skita, *Ber.*, 1915, **48**, 1486.]

1914. Anisaldehyde to anisyl alcohol with Voorhees-Adams' platinum oxide catalyst. As with salicyl aldehyde, which see.

1915. Anisaldehyde to anisyl alcohol. Ether, ethyl acetate, ethanol or methanol solution : platinum-black catalyst at 70°. Polymerization occurs at 97°. [Vavon, *Compt. rend.*, 1912, **154**, 359 (1912).]

1916. Vanillin to vanillyl alcohol, with Voorhees-Adams' platinum oxide catalyst. See under Benzaldehyde; use 160 cc. absolute alcohol, to which add 0.36 millimole of sodium ethylate before adding ferrous chloride.

1917. Vanillin to vanillyl alcohol. Liquid phase much more rapid in alcohol than in ether solution : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **154**, 359.]

1918. Methyl-vanillin to methyl-vanillyl alcohol. Liquid phase : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **154**, 359.] This reduction does not take place in ether but is rapid in methanol solution.

1919. Ethyl-vanillin to ethyl-vanillyl alcohol. Ethyl acetate solution : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **154**, 359.]

1920. Acetyl-vanillin with platinum-black in ether (Willstätter's method) yields the alcohol. [Vavon, *Compt. rend.*, 1912, **154**, 359.]

1921. Salicyl aldehyde to saligenin with Voorhees and Adams' platinum oxide catalyst; 95 per cent ethyl alcohol as solvent (see under Benzaldehyde). Before filtering off the platinum add 0.4 cc. *N* aqueous sodium hydroxide to prevent polymerization.

1922. Methyl-salicylic aldehyde to methyl-saligenin. Liquid phase : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **154**, 359.]

1923. Benzoyl vanillin to the alcohol. Alcohol or ether solution : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **154**, 359.]

1924. Benzoyl-salicylic aldehyde to saligenin. Liquid phase : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **154**, 359.]

1925. Ethyl 4-anisylhydantoin-*N*-1-propionates (2 isomers) were obtained by hydrogenation of ethyl 4-anisal-hydantoin-*N*-1-propionate. Alcoholic solution : colloidal palladium catalyst : ten hours shaking with hydrogen. [Hahn and Gilman, *J. Am. Chem. Soc.*, 1925, **47**, 2948.]

1926. $\gamma\gamma$ -Dimethoxy- $\alpha\gamma$ -dianisylpropylene on reduction with hydrogen and a palladium catalyst gives $\gamma\gamma$ -dimethoxy- $\alpha\gamma$ -di-*p*-anisyl-propane (dimethyl-acetal of anisyl- β -anisylethyl ketone). [Straus and Heyn, *Ann.*, 1925, **445**, 92.]

1927. δ -Benzoyl- γ -phenyl- $\beta\beta$ -dimethylbutylaldehyde to ϵ -hydroxy- $\gamma\epsilon$ -diphenyl- $\beta\beta$ -dimethyl valeraldehyde. Platinum-black catalyst.

1928. 2-Methoxy-4 : 6-diphenyl-3 : 3-dimethyl-3 : 4-dihydro-1 : 2-pyran to 2-methoxy-4 : 6-diphenyl-3 : 3-dimethyltetrahydropyran. [Meerwein, *et al.*, *J. pr. Chem.*, 1927, **116** (ii), 229.]

1929. Polyhydroxybenzyl Alcohols from Aldehydes.⁴ The catalytic reduction of the CO group was found to differ. The catalyst was palladium on barium sulphate. Protocatechualdehyde readily took up 2 molecules of hydrogen and gave homopyrocatechol. Dicarboxymethoxyprotocatechualdehyde yields the alcohol, while dicarbomethoxyprotocatechualdehyde was unaffected.

⁴ Rosenmund and Boehm, *Arch. Pharm.*, 1927, **264**, 448; *Chem. Abst.*, 1927, **21**, 2886.

1930. Gallic aldehyde absorbs slowly 1 molecule of hydrogen forming pyrogallol; tricarbomethoxygallic aldehyde rapidly took up 1 molecule of hydrogen. Tricarbomethoxygallic aldehyde also hydrogenated rapidly to the alcohol, but dicarbomethoxygallic aldehyde was unaffected.⁵

1931. Decomposition of complex aldehydes in contact with nickel above 200° C. [Mailhe, *Bull. Soc. Chim.*, 1926, **39**, 922; *Chem. Abst.*, 1927, **21**, 576.]

1932. Formation of Ethers from Acetals. Hydrogenation of benzaldehydediethylacetal at 180° by the Sabatier and Senderens process yields benzyl ethyl ether (45 per cent). From phenylacetaldehydedimethylacetal there is produced methyl β -phenylethyl ether (50 per cent).

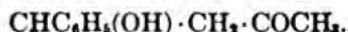
1933. Similarly, heptaldehydediethylacetal yields ethyl heptyl ether (61 per cent); heptaldehydedi-*n*-propylacetal, affords *n*-propyl heptyl ether (64 per cent); heptaldehydediisobutylacetal gives isobutyl heptyl ether (64 per cent); phenylacetaldehydedi-*n*-propylacetal furnishes β -phenylethyl *n*-propyl ether (80 per cent), and cinnamaldehydediethylacetal yields ethyl γ -phenylpropyl ether.⁶ [Sigmund and Marchart, *Monatsh.*, 1927, **48**, 267.]

1934. Hydrogenation of phenylacetaldehyde diethylacetal with platinum-black in anhydrous acetic acid yields, however, hexahydrophenylacetaldehyde diethylacetal and unreduced acetal, together with small quantities of liquids, b.p. 195°–202° (chiefly hexahydrophenylethyl ethyl ether) and b.p. 202–210° (probably a mixture of the latter ether and reduced acetal). Phenylacetaldehyde dimethylacetal under similar conditions gives an 81 per cent yield of hexahydrophenylacetaldehyde dimethylacetal, and a small quantity of a fraction of b.p. 194°–197° (probably a mixture of hexahydrophenylethyl methyl ether and the reduced acetal).⁷ [Sigmund, *Monatsh.*, 1928, **49**, 271.]

KETONES

1935. Carbonyl Group in Aromatic Compounds: Copper Catalyst under High Pressure. Aromatic ketones in these conditions give alcohols. Benzil at 100° and 76–92 atmospheres gives benzoin, hydrobenzoin and isohydrobenzoin. Benzoyl acetone at 83° gives β -hydroxy- β -phenylethyl methyl ketone and phenyl- β -hydroxy-*n*-propyl ketone; at 105° it gives α -phenyl-*n*-butane- $\alpha\gamma$ -diol. Phthalic anhydride gives hydrophthalyl-lactonic acid (benzyl-phthalide-*o*-carboxylic acid) and dihydroxyphthalan. [Kubota and Hayashi, *Sci. Papers Inst. Phys. Chem. Res.*, 1926, **5**, 1–6].

1936. The following^{7a} is from a different account of the same work. The results of Sabatier and his collaborators show that, under ordinary pressure, copper is a suitable catalyst for the dehydrogenation of the carbinol group, rather than for the hydrogenation of the carbonyl group. It was therefore expected that the reverse would be true under high pressure. This has been confirmed by Kubota and Hayashi, who, as indicated in para. 1935, heated various mono- and di-ketones, mixed with copper powder, in an autoclave. The pressure employed was 60–90 atmospheres. Acetophenone at 140° yielded phenylmethylcarbinol, and at 160° ethylbenzene. Benzophenone at 120° gave diphenylcarbinol and diphenylmethane, at 190° diphenylmethane and tetraphenylethane. Camphor at 120°–150° gave borneol and isoborneol. From benzil at 100°, benzoin (43 per cent), hydrobenzoin, and isohydrobenzoin were formed, while at 130° hydrobenzoin (74 per cent) and isohydrobenzoin (14 per cent) were the chief products. Benzoylacetone at 83° yielded, besides much unchanged starting material, 30 per cent of methyl β -hydroxy- β -phenylethyl ketone.



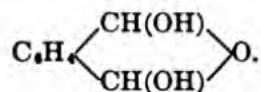
⁵ Cf. full abstract in *Brit. Chem. Abst.*, 1927, 1130A.

⁶ *Brit. Chem. Abst.*, 1927, 1054A.

⁷ *Brit. Chem. Abst.*, 1928, 1009A.

^{7a} Cf. *Brit. Chem. Abst.*, 1926, 520A.

At 105°, benzoylacetone was reduced mainly to γ -phenyl- α -methyltrimethylene glycol. Phthalic anhydride at 120° formed 70 per cent of *o*-carboxybenzylphthalide, together with 12 per cent of dihydroxyphthalan,



1937. Hydrogenation of Ketones with Pure and Impure Platinum-blacks. Failebin⁸ describes and discusses fully the effect of impurities such as iron, alumina, and silica. The effect is qualitative as well as quantitative. In this connection the earlier observations of Carothers and Adams⁹ should be noted.

1938. Acetophenone to ethyl benzene: above 250°, with nickel of only moderate activity. With active nickel at 180° the aromatic nucleus is hydrogenated, yielding ethyl-cyclohexane. But with partially inactivated nickel or at 300° C. this complication is avoided. [Darzens, *Compt. rend.*, 1904, **139**, 868.]

1939. Acetophenone to ethylbenzene. Gas phase: 420°: thoria catalyst; with excess of methanol vapor. [Sabatier and Murat, *Compt. rend.*, 1913, **157**, 1499; *Bull. Soc. Chim.*, 1914 (4), **15**, 227.] Acetophenone to ethylbenzene: 300°; with nickel or thoria; with vapors of formic acid. [Mailhe and de Godon, *Bull. Soc. Chim.*, 1917 (4), **21**, 61.]

1940. Ketones: Hydrogenation by Formic Acid.¹⁰ The vapors of formic acid passed over catalysts (e.g., platinum, copper, nickel, cadmium, stannous oxide, zinc oxide) at 200°–400° C., with the vapor of organic substances, exerts on these latter a reducing action due to its decomposition with liberation of hydrogen.¹¹ Aromatic ketones are smoothly reduced to the hydrocarbons: aliphatic ketones usually give the corresponding secondary alcohol, but acetone condenses to mesityl oxide and phorone. For the production of diphenyl-urea derivatives, the vapor of the RNH₂ is passed with formic acid over nickel at 400° C. HCONHR first formed decomposes at 360°, giving CO and an arylamine, but at 400° C. combination takes place and a CO(NHR)₂ results.

1941. Phenyl-ethyl-ketone to propylbenzene. Gas phase: 300°: nickel, copper, platinum, cadmium oxide, stannous oxide, zinc oxide, thoria, alumina or zirconia as catalyst, the last three above 300°. Vapors of the ketone and of formic acid are passed over the catalyst. The formic acid breaks down to hydrogen and carbon dioxide. [Mailhe and de Godon, *Bull. Soc. Chim.*, 1917 (4), **21**, 61.]

1942. Benzyl-acetone, C₆H₅·CH₂·CH₂·CO·CH₃ to butyl-benzene. Gas phase: over 250°: moderately active nickel catalyst. [Darzens, *Compt. rend.*, 1904, **139**, 868.]

1943. Benzoyl-acetone, C₆H₅·CO·CH₂·CO·CH₃ to butyl-benzene (80 per cent), toluene and isopropyl alcohol (*via* acetone). Gas phase: 200°: nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1907, **145**, 1126.]

1944. 2:4-Diethoxy-acetophenone to 2:4-di-ethoxy-ethylbenzene. Acetic acid solution: nickel catalyst.¹²

1945. Hydroxymethylene Derivatives of Ketones. In hydroxymethylene derivatives, the group >C:CHOH is changed to methyl >CH₂, when hydrogenated with a colloidal palladium (gum arabic) catalyst. [Koetz and Schaeffer, *J. prakt. Chem.*, 1913 (2), **88**, 604.] This is a means of methylation, e.g., camphor hydroxymethylene deriva-

⁸ *Ann. chim.*, 1925, **4**, 156, 410; *Chem. Abst.*, 1926, **20**, 740; *Compt. rend.*, 1926, **183**, 138; *Chem. Abst.*, 1926, **20**, 1218.

⁹ *J. Am. Chem. Soc.*, 1923, **45**, 1081.

¹⁰ Mailhe, *J. usines gaz.*, 1925, **49**, 147.

¹¹ Mailhe and de Godon, *Bull. Soc. Chim.*, 1917, (4), **21**, 61.

¹² Brit. Pat. application 256,225 (convention date July 30, 1925), by Hirszel, assignee of Schilt; *Chem. Age* (London), 1926, **15**, 356.

tive hydrogenated in glacial acetic acid solution gives methyl-camphor, and from cyclohexanone methyl cyclo-hexanone can similarly be obtained.¹⁴

1946. Piperonal acetone to saturated ketone. Ethyl acetate solution: platinum-black catalyst. [Vavon and Faillebin, *Compt. rend.*, 1919, **169**, 65.]

1947. Dipiperonal-acetone to the saturated ketone. Ethyl acetate solution: platinum-black catalyst. [Vavon and Faillebin, *Compt. rend.*, 1919, **169**, 65.] The reaction has two phases: the first product is the mono-ethylenic ketone.

1948. Isobutylideneacetone to methylisoamylketone. [Chavanne, *Bull. Soc. Chim. Belg.*, 1927, **36**, 206.]

1949. Vanillidene-acetone to vanillyl-acetone and the secondary alcohol: $\text{HO}(\text{CH}_2\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$. Palladium animal charcoal catalyst. This alcohol is converted by 60 per cent sulphuric acid into homoeugenol. [Mannich and Merz, *Arch. Pharm.*, 1927, **265**, 104; *C. A.*, 1927, **21**, 1803.]

1950. 4-Hydroxy-3-methoxystyryl-ethyl ketone (produced by condensation of vanillin with methyl-ethylketone) to 4-hydroxy-3-methoxyphenylethyl-ethyl ketone. Platinum-black catalyst. [Ichikawa, *Sci. Rep. Tohoku*, 1925, **14**, 127, *J.S.C.I.*, 1925, B, 736.]

1951. Di-4-hydroxy-3-methoxystyryl ketone (condensation product of vanillin and acetone) to di- β -4-hydroxy-3-methoxy-phenylethyl ketone. Platinum-black catalyst. [Nomura and Hotta, *Sci. Rep. Tohoku Imp. Univ.*, 1925, **14**, 119.]

1952. Cyclohexanone in the gas phase, over nickel, below 180° , hydrogenates to cyclohexanol and a small quantity of cyclohexane. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 402.] In ethereal solution (50 per cent) with platinum-black catalyst the same result is obtained. [Vavon, *Compt. rend.*, 1912, **155**, 287.]

1953. Methyl-cyclohexanones to methyl-cyclohexanols (and small quantities of the methyl-cyclohexanes). Gas phase: below 180° : nickel catalyst. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 402.] The methyl-cyclohexanones in 5 volumes of ether, can be reduced to the methyl-cyclohexanols, by hydrogenation in the presence of platinum-black catalyst. [Sabatier: *Catalysis*, 567.]

1954. Allylation of cyclohexanones. The allyl products can be hydrogenated to the corresponding normal propyl compounds. [Cornubert and Le Bihan, *Bull. Soc. Chim.*, 1927, **41** (iv), 1077.]

1955. Unsaturated 2, 5-substituted cyclohexanones to the corresponding saturated cyclohexanones, with Voorhees-Adams platinum oxide catalyst. Suspension in ethyl alcohol (95 per cent); 1-2 atmospheres hydrogen pressure: 1 g. catalyst to 250 cc. alcohol. The quantity of each unsaturated ketone used is given in grams after the name of the saturated ketone in the following list: Dibenzyl-cyclohexanone (20), di-*p*-methylbenzyl-cyclohexanone (8), di-2, 4-dimethylbenzyl-cyclohexanone (1.55), di-*p*-chlorobenzyl-cyclohexanone (5), dianisyl (4), dipiperonyl (20). [Garland and Reid, *J. Am. Chem. Soc.*, 1925, **47**, 2333.]

1956. Methyl-*para*-cresyl-ketone to *para*-methyl-ethyl-benzene. Gas phase: above 250° (if at a lower temperature, the catalyst must be inactive toward the aromatic nucleus): nickel catalyst. [Darzens, *Compt. rend.*, 1904, **139**, 868.]

1957. Benzoin, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_5$, to dibenzyl, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$. Gas phase: 210° - 220° : nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1907, **145**, 1126.]

1957A. For the catalytic hydrogenation of alpha-diketones and their derivatives by Adams' method see Buck and Jenkins (*J. Am. Chem. Soc.*, 1920, **51**, 2163). The reduction of the following substances is described (the name of the product is given in parentheses): benzil (benzoin and hydro-benzoin); anisil (anisoin and hydro-anisoin); piperil (piperoin and hydro-piperoin); desoxybenzoin (toluylene hydrate); desoxy-anisoin (di-*p*-methoxy-toluylene hydrate); desoxypiperoin (di-*p*-methylene-dioxy-toluylene hydrate); stilbene (diphenylethane); di-*p*-methoxystilbene (di-*p*-methoxydiphenylethane); di-*p*-methylenedioxystilbene (*d-p*-methylenedioxydiphenylethane).

¹⁴ For reduction products of hydroxymethylene-aceto-phenone and of 1-hydroxymethylene-1-benzylacetone, see Rüpe and Muller. *Helv. Chim. Acta*, 1921, **4**, 841; *Chem. Abst.*, 1922.

1958. Benzyl to benzoin. Ten per cent solution in alcohol : colloidal palladium catalyst : atmospheric pressure. [Borsche and Walter, *Ber.*, 1926, 59, 464.]

1959. Dibenzoyl, in gas phase, over nickel, at 220° gives dibenzyl (symm. diphenylethane). [Sabatier and Mailhe, *Compt. rend.*, 1907, 145, 1126.]

1960. Benzophenone to diphenylmethane. Gas phase : 300° : nickel catalyst, preferably of only moderate activity. Instead of hydrogen, the vapors of formic acid may be used, with nickel, thorium, alumina or zirconia as catalysts. [Mailhe and de Godon, *Bull. Soc. Chim.*, 1917 (4), 21, 61] or methanol vapor [Sabatier and Murat, *Bull. Soc. Chim.*, 914, (4), 15, 227.]

1961. By Ipatiev's method, with nickel oxide catalyst, diphenylmethane is formed. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 491; *Chem. Centr.*, 1908 (2), 1098.]

1962. Over copper (of a violet tint, prepared by reduction of the hydroxide) at 350°, diphenylmethane is also produced. [Sabatier and Murat, *Compt. rend.*, 1914, 158, 761.]

1963. To dicyclohexyl-methane. By the use of colloidal platinum at 60°, benzophenone is hydrogenated to dicyclohexyl-methane. [Skita, *Ber.*, 1915, 48, 1486.] The same result is obtained in the gas phase, by the use of an active nickel catalyst at 160°. To diphenylcarbinol, with very active platinum black in ether solution. [Vavon, *Compt. rend.*, 1912, 155, 287.]

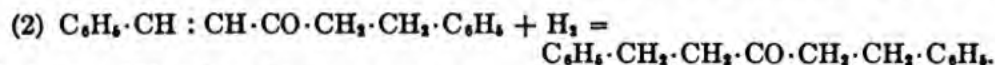
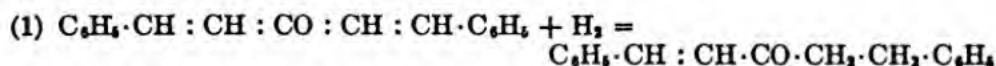
1964. Benzoyl-phenylethylene to benzoyl-phenylethane. Acetone solution : slight plus pressure : colloidal palladium catalyst. The hydrogenation continues with formation first, of diphenyl-ethyl-carbinol, second, of diphenyl-propane. Not all related aromatic and hydroaromatic carbonyl compounds were found to be hydrogenated in this manner. A large number of substances was subjected to this hydrogenation, for details of which the original paper should be consulted. [Straus and Grindel, *Ann.*, 1924, 439, 276.]

1965. Distyrylketone to di-β-phenylethylketone. Ipatiev's method. Benzene solution : nickel oxide catalyst.

1966. Di-β-phenylethylketone to αα-di-cyclohexyl pentane. Ipatiev's method at 240° C. [Ipatiev and Orlov, *Compt. rend.*, 1927, 184, 751.]

1967. Diphenylethanone (desoxybenzoin, $C_6H_5 \cdot CO \cdot CH_2 \cdot C_6H_5$) to diphenylethane (dibenzyl). Gas phase : over nickel : 350° C. [Sabatier and Murat, *Ann. Chim.*, 1915, (9), 4, 263.]

1968. Dibenzylidene-acetone (dibenzalacetone), in benzene solution diluted with alcohol, by Paal's method, with colloidal palladium gives, first, benzyl-benzylidene-acetone, and then, dibenzyl-acetone.



[Paal, *Ber.*, 1912, 45, 2221.]

1969. By Ipatiev's method with 15 per cent nickel oxide, dibenzalacetone in benzene solution, heated for twenty-four hours, at 170°–180° C. and under 70–180 atmospheres hydrogen pressure, gave dibenzylacetone. The dibenzylacetone dissolved in cyclohexane and heated with the same catalyst for twelve hours at 240° C. gave 1, 5-dicyclohexyl-pentane. [Ipatiev and Orlov, *J. Russ. Phys. Chem. Soc.*, 1927, 59, 537; also in: *Compt. rend.*, 1927, 184, 751; *Chem. Abst.*, 1927, 21, 1974.]

1970. Benzalacetophenone (benzylidene acetophenone) to benzylacetophenone. Liquid phase : ethyl acetate solution : Adams' platinum catalyst, fifteen to twenty minutes at room temperature. [*Organic Syntheses*, 1928, 8, 36. See also Straus and Grindel, *Ann.*, 1924, 439, 294. (Palladium catalyst.)]

1971. Arylamino-alkylketones to the carbinols. Nickel catalyst, on pumice. *Examples*: *N*-methylamino-acetophenone to phenyl-*N*-methyl-aminomethyl-carbinol : amino-acetophenone to phenylamino-methylcarbinol : *N*-methylamino-propiofenone to phe-

nyl-*N*-methylamino-ethyl-carbinol : ω -methylamino-aceto-pyrocatechin to racemic adrenalin.¹⁴

1972. For the same hydrogenations,¹⁵ are used an alkaline solution, a nickel or a platinum group catalyst and the exclusion of oxygen. [*Chem. Age* (London), 1928, **19**, 419.]

1973. Cyclic Ketones: Relative Reactivity in Hydrogenation.¹⁶ The relative ease of reduction of cyclic ketones with hydrogen and platinum-black is determined by reduction of equimolecular mixtures of an optically inactive ketone and menthone with only one molecular proportion of hydrogen, the partition of the hydrogen between the two ketones being followed by measurements of optical activity. The results show that a substituent in position 2 diminishes the ease of hydrogenation, the effect being more marked for isopropyl than for *n*-propyl groups. The order of reactivity is: cyclohexanone, 4-methyl-, 2-methyl-, 2-propyl-, 2-iso-propyl-, 2-cyclohexyl-cyclohexanones, menthone, cyclo-pentanone, 2-isopropylcyclopentanone, camphor, fenchone.¹⁷

1974. Hydrogenation of Synthetic Ketones. Ketones obtained by condensation of benzal-acetone (benzylidene-acetone, styryl-methyl-ketone, $C_6H_5CH : CH \cdot CO \cdot CH_3$) or piperonylidene acetone ($CH_3O_2C_6H_3CH : CH \cdot CO \cdot CH_3$) with formaldehyde and a secondary amine (diethylamine or ethylpropylamine) on hydrogenation with palladium-charcoal catalyst are affected only at the double linkages in the side (open) chain. E.g., Piperidinophenylpentenone to piperidinophenylpentanone. Diethylaminophenylpentenone to diethylaminophenylpentanone. Piperidino-5-[3, 4-methylenedioxyphenyl]-4-pentenone to piperidino-5-[3, 4-methylenedioxyphenyl]-4-pentanone. Piperidino-5-[3, 4-dimethoxyphenyl]-4-pentenone to piperidino-5-[3, 4-dimethoxyphenyl]-4-pentanone. Diethylamino-5-[3, 4-methylenedioxyphenyl]-4-pentenone to diethylamino-5-[3, 4-methylenedioxyphenyl]-4-pentanone. Piperidino-5-[*p*-methoxyphenyl]-4-pentenone to piperidino-5-[*p*-methoxyphenyl]-4-pentanone. [Mannich and Schütz, *Arch. Pharm.*, 1928, **265**, 684; *Chem. Abst.*, 1928, **22**, 963.]

1975. Dibenzalacetone-dimethyl-acetal to dibenzylacetone-dimethyl-acetal. [Straus and Heyn, *Ann.*, 1927, **458**, 256; *C. A.*, 1928, **22**, 407.]

1976. Benzylidenethebainone to benzylthebainone (2 isomers). Liquid phase: palladium chloride. [Gulland, *J. Chem. Soc.*, 1928, 702.]

1977. Xanthone hydrogenated under pressure at 200° C. in presence of nickel salts gives various products: xanthene, hexahydroxanthene (?-tetrahydroxanthene), dodecahydroxanthene, *o*-hexahydrobenzyl-cyclohexanol, dodecahydrodiphenylmethane. [V. Braun and Bayer, *Ber.*, 1926, **59B**, 2317.] See also: Ipatiev and Orlov, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1034.

1978. The ketone, $C_{14}H_{14}O_2$, obtained by oxidation of *p*-cresol with potassium ferricyanide, hydrogenated with spongy platinum catalyst gives an alcohol $C_{14}H_{16}O_2$. [Pummerer, Puttfarcken, Schopflocher, *Ber.*, 1925, **58B**, 1808.]

1979. Anhydroepicatechin-tetramethyl ether to deoxyepicatechin-tetramethyl ether. Platinum catalyst. The product probably has the structure of a tetramethoxybenzylcoumarone.

1980. *mp*-Dimethoxybenzylidene-coumarone to dimethoxybenzylcoumarone. Nickel catalyst. [Freudenberg, Fikentscher and Harder, *Ann.*, 1925, **441**, 157.]

1981. 7-Acetoxychromone to 7-acetoxychromanone. Acetic acid solution. [Pfeiffer, Oberlin and Konermann, *Ber.*, 1925, **58B**, 1947.]

1982. Santonin to tetrahydrosantonin. In glacial acetic acid solution : platinum-black catalyst. [Asahina, *Ber.*, 1913, **46**, 1775.] Sodium santonate is, likewise, hydrogenated to sodium tetrahydrosantonate in presence of platinum-black catalyst. Cusimano, *Lincei*, 1913, **22**, 507.]

¹⁴ Brit. Pat. application 280,574, convention date, Nov. 10, 1926, to Merck; *Chem. Age* (London), 1928, **18**, 85; Ger. Pat. 469,782, Nov. 11, 1926; *Chem. Abst.*, 1929, **23**, 1416.

¹⁵ Brit. Pat. 296,006, Aug. 22, 1927, to Soc. Chem. Ind. Basle; *Chem. Abst.*, 1929, **23**, 2187.

¹⁶ Vavon and Couderc, *Bull. Soc. chim. Belg.* (1927), **36**, 57.

¹⁷ *Brit. Chem. Abst.*, 1928, 547A.

1983. Elemol on ozonization gives (among other products) a ketone $C_{14}H_{22}O$, which, on catalytic hydrogenation, gives the alcohol $C_{14}H_{24}O$.

1984. Campnospermonyl methyl ether to tetrahydrocampnospermonyl methyl ether. Ether solution: platinum oxide ("dioxide") catalyst. Reduction of the tetrahydro ether with zinc and hydrochloric acid gives an unsaturated methoxy-hydrocarbon ($?C_{28}H_{46}O$), which, with platinum catalyst is hydrogenated to a saturated methoxy-hydrocarbon ($?C_{28}H_{50}O$).

Campnospermonyl acetate by hydrogenation with platinum oxide ("dioxide") catalyst affords tetrahydrocampnospermonyl acetate.

The parent body, campnospermonol, is a ketonic phenol derived from the oil of *Campnospermum brevipetiolatum*, and appears to be either β -*m*-hydroxy-phenyl- $\Delta^{\alpha\mu}$ -heneicosadien- δ -one: $OH \cdot C_6H_4 \cdot C(: CH_2) \cdot CH_2 \cdot CO \cdot [CH_2]_7 \cdot CH : CH \cdot [CH_2]_7 \cdot CH_3$, or β -*m*-hydroxybenzyl- $\Delta^{\alpha\mu}$ -heneicosadien- δ -one. [Jones and Smith, *J. Chem. Soc.*, 1928, 65.]

1985. 2- γ -Ketobutenylnaphthalene to 2- γ -ketobutylnaphthalene. Acetic acid suspension: colloidal platinum: 2 atmospheres. 1- γ -ketobutenylnaphthalene to 1- γ -ketobutylnaphthalene. [Gibson *et al.*, *J. Chem. Soc.*, 1926, 2247.]

1986. Methyl-naphthyl-ketones to ethyl-naphthalenes. Gas phase: 180°: nickel catalyst. [Darzens and Rost, *Compt. rend.*, 1908, 146, 933.] In general: naphthylalkyl ketones to alkyl naphthalenes.

1987. Benzylidene- α -tetrahydronaphthalene ketone to benzyl- α -tetrahydronaphthalene ketone: platinum-black: acetic acid solution.¹⁸

1988. Anthraquinone is hydrogenated with ease, in decalin solution, at 200° with a nickel catalyst and 10–15 atmospheres pressure. If the supply of hydrogen is controlled a quantitative yield of anthranol is obtained. Further addition of hydrogen gives 1:2:3:4-tetrahydroanthranol and 1:2:3:4:5:6:7:8-octahydroanthranol.

1989. Dihydroanthranol is hydrogenated in these conditions to 1:2:3:4-tetrahydroanthranol (15 per cent) 9:10-dihydroanthracene and 1:2:3:4-tetrahydroanthracene. This confirms the view that the primary product of the hydrogenation of anthracene is 9:10-dihydroanthracene and that this passes into 1:2:3:4 tetrahydroanthracene. Whether catalytic hydrogenation of anthracene occurs exclusively through the 9:10-dihydro-compound or whether the primary attack takes place also at the side nucleus cannot be decided for the hydrocarbon, but a decision can be reached from its oxygenated derivatives, using anthranol as starting-point; if hydrogenation occurs initially in the 9:10-position, the yield of tetrahydroanthranol from this substance cannot, under identical conditions, exceed that from dihydroanthranol. Actually the yield is far greater, so that for anthranol the primary attack occurs mainly or possibly exclusively at the side nucleus. The possibility that tetrahydroanthranol is readily attacked by hydrogen with elimination of the hydroxy-group and formation of tetrahydroanthracene is invalidated by the observation that it absorbs hydrogen less readily than anthranol or dihydroanthranol and yields successively 1:2:3:4:5:6:7:8-octahydroanthranol and 1:2:3:4:5:6:7:8-octahydroanthracene.

1990. Anthraquinone Derivatives and Benzanthrone. *Hydrogenation in vapor phase.* The substrate, preferably mixed with copper or zinc dust, is sublimed with a current of hydrogen over a catalyst (e.g., a mixture of reduced copper and zinc) at 325°–475° C., according to the catalyst and the substrate. 2-Aminoanthraquinone at 460°–475° C. gives 2-aminoanthracene. Similarly are obtained: 1-aminoanthracene; 2-methylaminoanthracene; 1-diethylamino-anthracene; 2:6-dimethoxyanthracene; 2-methylanthracene.¹⁹

1991. 2-Acetamidoanthraquinone to 2-acetamido-9, 10-anthrahydroquinone (this is readily oxidizable and it is converted into 2-acetamido-9, 10-anthrahydroquinone-

¹⁸ Riedel, A. G., Ger. Pat. 422,036, 1923.

¹⁹ Brit. Pat. 260,000, Oct. 18, 1926 (Ger. Pat., Oct. 17, 1925) to the I. G., assignees of Farb. vorm. Meister, Lucius and Brüning.

dimethyl ether, by acting on it with methyl sulphate in alkaline solution). 2-acetamidoanthraquinone (26.5 parts) suspended in alcohol (200 parts) plus nickel catalyst (2 parts) : hydrogen pressure 20 atmospheres : agitation. The reaction is exothermic.²⁰

1992. Acylaminoanthraquinones to 2-acylamino-*ms*-dihydroxyanthracenes. Solution in pyridine or chlorbenzene, or suspension in alcohol, or in aqueous alkali : nickel catalyst : hydrogen pressure 20 atmospheres.²¹

1993. Indanthrone Dye Intermediate. 2-Acetamidoanthraquinone to dimethyl ether of *leuco-β*-aminoanthraquinone. Nickel catalyst.²²

1994. Hexahydroanthrone to octahydroanthracene. Gas phase : 200° : nickel catalyst. [Godchot, *Bull. Soc. Chim.*, 1907 (4), 1, 712.]

²⁰ Can. Pat. 283,918, Oct. 9, 1928, to Schirmacher, Schlichenmaier, Kross, Schaich, Tampke and Neumann (assigned to I. G. Farbenind. A.-G.); *Chem. Abstr.*, 1929, **23**, 607.

²¹ Brit. Pat. 297,042, Apr. 13, 1927, to Imray, as agent for I. G. Farbenind. A.-G.

²² Brit. Pat. 279,401, Aug. 26, 1927, to I. G. Farbenind. A.-G. Ger. Pat. date, Oct. 21, 1926.

CHAPTER XX

NUCLEAR HYDROGENATIONS OF CARBOCYCLIC COMPOUNDS

CARBOCYCLIC NUCLEI WITH MORE OR LESS THAN SIX CARBON ATOMS

2000. Cyclopropane. Cyclopropane, in gas phase, over nickel, at 120°, yields propane. [Willstätter and Bruce, *Ber.*, 1908, **40**, 4456.]

2001. Methylcyclopropene gives isobutane in the gas phase, over nickel, at 170°–180° C. [Mereshkovski, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 97; *Chem. Abst.*, 1914, **8**, 1965.]

2002. Ethyl cyclopropane to isopentane. Gas phase over nickel. [Rozanov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 168; *Chem. Abst.*, 1917, **11**, 454.]

2003. Dimethylmethylene-cyclopropane to isohexane. Gas phase : 160° : nickel catalyst. [Zelinsky, *Ber.*, 1907, **40**, 4743.]

2004. 3-Methylcyclopropene-1 : 2-dicarboxylic acids (A or B) to 3-methylcyclopropane-1 : 2-dicarboxylic acids (2 isomers, m.p. 147° and 108°.) Colloidal palladium catalyst. [Feist, *Ann.*, 1924, **436**, 125.]

2005. Cyclobutene in gas phase, over nickel, at 100°, gives first cyclobutane, then at 180° butane. [Willstätter and Bruce, *Ber.*, 1907, **40**, 3979–3980.]

2006. Cyclopentadiene in gas phase, over nickel, at 180°, yields cyclopentane. [Eijkman, *Chem. Weekblad.*, 1903, **1**, 7.]

2007. 1, 3-Dimethyl-1-cyclopentene to inactive 1, 3-dimethylcyclopentane. Acetic acid solution : platinum-black catalyst. Synthesis of the olefine is described. [Chavanne, *Bull. sci. acad. roy. Belg.*, 1926 (5), **12**, 105.]

2008. 1, 2-Dimethyl-1-cyclopentene to 1, 2-dimethylcyclopentane. Platinum-black catalyst : 99 per cent yield. [Chavanne and Devogel, *Bull. soc. chim. Belg.*, 1928, **37**, 141.]

2009. 1-Ethyl-1-cyclopentene to ethyl-cyclopentane. 1-Propyl-1-cyclopentene to propyl-cyclopentane. 1-Butyl-1-cyclopentene to butyl-cyclopentane. Acetic acid solution : platinum-black catalyst. [Chavanne and Becker, *Bull. soc. chim. Belg.*, 1927, **36**, 591; *Chem. Abst.*, 1928, **22**, 1957.]

2010. Methylcyclopentenolone phenylurethane in alcoholic solution, in presence of palladium-charcoal catalyst, takes up 1 molecule of hydrogen, giving a product m.p. 90°–95°.

2011. 2-Methoxy-1-methyl- Δ^1 -cyclopenten-3-one hydrogenated in the same way yields 2-methoxy-1-methyl- Δ^1 -cyclopentan-3-one.

2012. Methylcyclopentenolone is reduced to methylcyclopentanone. [Rojahn and Rühl, *Arch. Pharm.*, 1926, **264**, 211.]

2013. The methyl ester of 4-methyl-1-isopropyl-1-cyclopentene-3-one-4-carboxylic acid to the ester of 4-methyl-1-isopropyl-3-cyclopentanone-4-carboxylic acid. In alcoholic solution, slowly with platinum sponge catalyst, more easily with colloidal platinum. 4-Methyl-1-isopropyl-1-cyclopentene-3-one (methyltanacetophorone) gives 4-methyl-1-isopropyl-3-cyclopentanone. [Toivonen, *Ann. acad. sci. Fennicae*, **A28**; *Chem. Abst.*, 1929, **23**, 1624.]

2014. 5-Benzoyloxy-2 : 2 : 3 : 3-tetramethyl- Δ^1 -cyclopentenone to a dihydro-derivative, $C_{16}H_{20}O_2$. Acetic acid solution : palladinized barium sulphate catalyst [1.9 g. ketone to 0.5 g. palladium). [Ingold and Shoppee, *J. Chem. Soc.*, 1928, 1871.]

2014A. 5-*p*-Bromobenzoyloxy-2 : 2 : 3 : 3-tetramethyl- Δ^1 -cyclopentenone even at 2

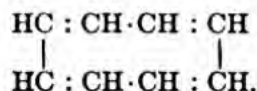
atmospheres pressure gave a substance m.p. 26°–27° C. too small in quantity for identification. For the most part the ketone was unchanged. [*Ibid.*]

2015. Chaulmoogric acid to dihydrochaulmoogric acid. 17 per cent solution in 95 per cent alcohol : palladium-platinum catalyst. Esterification occurs simultaneously.

2016. Hydnocarpic acid yields an optically inactive dihydrohydnocarpic acid. [Dean, Wrenshall and Fujimoto, *U. S. Pub. Health Service Bull.*, 1924, **141**, 24.]

2017. Cycloheptadiene, C_7H_{10} , to cycloheptane. Gas phase : 180° : nickel catalyst. If the operation is conducted at 235° the cycloheptane seems to undergo a molecular rearrangement to the isomer methyl-cyclohexane. [Willstätter and Kametaka, *Ber.*, 1908, **41**, 1480.]

2018. Cyclo-octatetrene in the gas phase over platinum forms cyclooctane. [Willstätter and Waser, *Ber.*, 1911, **44**, 3423.] Also with platinum-black [*Ibid.*, 3434.] Cyclo-octatetrene is:



2019. Bicyclo-octene (b.p. 1500) to bicyclo-octane (b.p. 140°). Gas phase : 150° : nickel catalyst. [Willstätter and Kametaka, *Ber.*, 1908, **41**, 1485.]

2020. Cyclooctenone in the liquid phase, with platinum-black catalyst (10 per cent, by weight) is converted into cyclooctanone. [Willstätter and Waser, *Ber.*, 1911, **44**, 3434.]

2021. Hexahydroindene and derivatives—stereochemistry. Hückel and Friedrich, *Ann.*, 1926, **451**, 132; *J.S.C.I.*, 1926, 238A.

2022. 1-Methyl- Δ^1 -cyclopentadecene to methylcyclopentadecane. Platinum-black catalyst. [Ruzicka, Schinz and Pfeiffer, *Helv. Chim. Acta*, 1928, **11**, 686.]

SIX-MEMBERED RINGS

HYDROCARBONS

2023. Experiments of Sabatier.¹ The special power of reduced nickel observed by Sabatier seemed so perfect that he thought of generalizing it, and hence attacked a case of hydrogenation, which up to that time had not been realized by any method, namely, that of benzene. Berthelot had attempted to effect it with his universal agent of hydrogenation, a concentrated solution of hydriodic acid at 250° C. But instead of cyclohexane, which boils at 81° C., Berthelot had prepared only its isomer, methylcyclopentane, which boils at 69° C. Under the influence of the hydriodic acid the hexagonal nucleus was transformed into a substituted pentagonal nucleus.

2023A. Hence Sabatier was led to make the following experiment: Benzene vapors, carried along by a current of hydrogen in excess, were directed over a bundle of reduced nickel, maintained at 200° C.; the gases issuing from the tube were sent to a U-tube surrounded by ice, within which the vapors of cyclohexane should be expected to condense to a liquid state. At the beginning, the velocity of hydrogen issuing from the condenser tube seemed very little less than that at the entrance. But after boiling for a rather short time the gas ceased to pass, the U-tube was stopped up by the condensation of a solid product, which it seemed could only be benzene, solidifiable at 4° C. Sabatier had seen in the literature that cyclohexane, extracted from Caucasian petroleum by Markovnikov was condensed to a solid which melted at –11° C.) On opening the U-tube, however, Sabatier perceived, instead of the odor of the original benzene, the special intermediate odor between that of chloroform and that of the rose, which belongs to cyclohexane. The condensed product was cyclohexane, entirely pure, melting not at –11° C. but above 6° C., absolutely unattacked by sulphonating reagent. The transformation of benzene by Sabatier's procedure had been complete.

2024. Benzene to Cyclohexane. Gas phase : nickel catalyst: 70°–190°. The hydrogenation is rapid at the higher temperatures, and without side reactions. Unchanged

¹ Sabatier, *Ind. Eng. Chem.*, 1926, **18**, 1006.

benzene may be removed by treating with a mixture of 1 volume fuming nitric acid and 2 volumes concentrated sulphuric acid. Above 190° and especially above 300°, methane is formed and carbon is deposited on the nickel. [Sabatier and Senderens, *Compt. rend.*, 1901, 132, 210.] At 250° and especially above 300° dehydrogenation occurs with regeneration of the benzene.

2024A. According to Sabatier and Senderens [*Ann. Chim. Phys.*, 1905 (8), 4, 367], fresh platinum-black catalyzes somewhat the hydrogenation of benzene to cyclohexane at 180°, but is rapidly put out of action by poisons. Platinum sponge was found inactive. Zelinsky affirms that both platinum and palladium are as efficient as nickel in this and other hydrogenations of the aromatic nucleus. [Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 274.] Colloidal platinum catalyzes this reaction "more or less readily" (Sabatier). Cobalt also catalyzes the hydrogenation of benzene at 180°, but soon loses its activity. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), 4, 368.]

2025. Adams' platinum oxide-platinum-black catalyst gave excellent hydrogenation of the compounds listed below.²

REDUCTION OF AROMATIC COMPOUNDS IN 50 CC. OF GLACIAL ACETIC ACID AT 25°-30°
TEMPERATURE AND 2-3 ATMOSPHERES PRESSURE

Compound Used	B. P., °C.	M. P., °C.	Amount of Substance, G.	Amount of Catalyst, G.	Time, hrs.
Benzene.....	79.5-80	15.6 (0.2 mole)	0.2	2.0
Toluene.....	110-111	18.4 (0.2 mole)	.2	2.75
Ethylbenzene.....	136-136.8	21.2 (0.2 mole)	.2	7.5
<i>m</i> -Xylene.....	139-140	21.2 (0.2 mole)	.2	21.5
Mixed xylenes.....	138-145	21.2 (0.2 mole)	.2	26.0
Mesitylene.....	164.5-166	12 (0.1 mole)	.2	8.5
Cymene.....	175-176.2	13.4 (0.1 mole)	.2	7.5
Diphenylmethane.....	27	16.8 (0.1 mole)	.2	7.0
Triphenylmethane*.....	92.2-92.5	8.74 (0.033 mole)	4 × 0.2	48.0
α , α -Diphenylethane.....	147 (15 mm.)	18.2 (0.1 mole)	3 × 0.2	26.5
Dibenzyl.....	52.5-53	18.2 (0.1 mole)	3 × 0.2	37.0
Phenylacetic acid.....	76	13.6 (0.1 mole)	.2	5.5
β -Phenylpropionic acid..	48	15.0 (0.1 mole)	.2	6.0

Compound Obtained	B. P., °C.	n_D	d	Ref.
Cyclohexane.....	79-79.5 (752 mm.)	1.4242/20°	0.7769/20°	7, 3, 4
Methylcyclohexane.....	100-100.2 (742 mm.)	1.4198/20°	.7687/20°	7, 4
Ethylcyclohexane.....	129.8-130 (743 mm.)	1.4278/25°	.7899/25°	8
<i>m</i> -Dimethylcyclohexane.....	118.5-119 (747 mm.)	1.4230/25°	.773/25°	3b, 9, 10
Mixed dimethylcyclohexanes....	118-123 (743 mm.)
Trimethylcyclohexane.....	135.5-136 (743 mm.)	1.4257/25°	.8250/25°	9
1-Methyl-4-isopropylcyclohexane	63 (22 mm.)	1.4370/25°	.8061/25°	9
Dicyclohexylmethane.....	110-110.5 (18 mm.)	1.4875/20°	.8884/20°	11
Tricyclohexylmethane.....	163.2 (4 mm.)	1.5264/20°	.9644/20°	12, 13
α , α -Dicyclohexylethane.....	112 (7 mm.)	1.4887/25°	.9070/25°	7, 14
α , β -Dicyclohexylethane.....	147-148.5 (12 mm.)	1.4760/18°	.8774/18°	4
Cyclohexylacetic acid.....	110-112 (3 mm.)	1.4558/30°	1.007/30°	16
β -Cyclohexylpropionic acid.....	112-114 (4 mm.)	1.4596/25°	1.0178/25°	15, 17

* Temperature 60° C.; 100 cc. of acetic acid.

² Adams and Marshall, *J. Am. Chem. Soc.*, 1928, 50, 1972.

2026. By Ipatiev's method, using 8 per cent of "nickel oxide," at 250°, benzene is quantitatively hydrogenated to cyclohexane. The nickel sesquioxide [sic] is said to give better results than the monoxide. Above 300° decomposition occurs with formation of benzene, carbon and methane. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 681-693; *Chem. Abst.*, 1907, **1**, 2877 and 2878.]

2027. Benzene to cyclohexane. Gas phase: 140°: active copper catalyst, produced by slow reduction from the oxide at 150°-300°. Excess of benzene inhibits the reaction; this is explained as due to hydrogen adsorption being blocked by preferential adsorption of benzene: maximum reduction obtained at 230° C. [Pease and Purdum, *J. Amer. Chem. Soc.*, 1925, **47**, 1435.]

2028. Cyclohexene, in liquid phase, with nickel catalyst is reduced to cyclohexane, at 160°-180° C. [Sabatier, **587**.]

2029. The Equilibrium between Benzene, Hydrogen and Cyclohexane. Burrows and Lucarini, *J. Am. Chem. Soc.*, 1927, **49**, 1157. Using a platinum catalyst (nickel having given erratic results owing to side reactions) the equilibrium constants were determined; at 266.5° C. the constant was 5.47 atmospheres and at 280° C., 1.62 atmospheres. These figures are of the same order of magnitude as those predicted from the Nernst approximation formula. [*Chem. Abst.*, 1927, **20**, 2213.]

2030. Some High-temperature Reactions of Benzene and Toluene in presence of hydrogen or of an inert gas. [Dufton and Cobb, *Gas. T.*, 1920, **150**, 588; *Gas World*, 1920, **72**, 485; *Chem. Abst.*, 1920, 2614.]

2031. Toluene to methyl-cyclohexane. Gas phase: 150°-180° (below 250°): nickel catalyst. Residual traces of toluene removed by shaking with mixture of 1 volume fuming nitric acid to 2 volumes of concentrated sulphuric acid. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 568.]

2032. Freshly prepared platinum-black can be used to catalyze the hydrogenation, at 180°, of toluene to methyl-cyclohexane. According to Zelinsky, it is as efficient for this purpose as is nickel, but Sabatier reports that the activity of the catalyst rapidly wanes. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 368; Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 274.]

2033. In acetic acid solution, with a colloidal palladium catalyst, toluene is hydrogenated to methyl-cyclohexane. [Skita, *Ber.*, 1915, **48**, 1486.] The same hydrogenation may be effected with a platinum-black catalyst. [Halse, *J. prakt. Chem.*, 1915 (2), **92**, 40.] Rhodium (but not ruthenium) black may also be used, but it is not very active. [Madinaveitia, *Soc. Esp. Fis. Quím.*, 1913, **11**, 328.]

2034. Xylene (*ortho*-, *meta*-, or *para*-) to *ortho*-, *meta*, or *para*-dimethyl-cyclohexane. Gas phase: 180°: nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 568.]

2035. Dimethyl-cyclohexenes to corresponding dimethyl-cyclohexanes. Gas phase: below 180°: active nickel catalyst. [Sabatier and Mailhe, *Ann. Chim. Phys.*, 1907 (8), **10**, 555.]

2036. Cinnamene (phenyl-ethylene or styrene) to ethyl-cyclohexane. Gas phase: 160°: active nickel catalyst. With less active nickel at 200°, ethyl benzene is the chief product. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1255.] Even with active nickel ethyl-benzene is produced at 300° C. [Sabatier and Murat, *Compt. rend.*, 1913, **156**, 184], as also with a copper catalyst at 180° C.

2037. Ethyl-benzene to ethyl-cyclohexane (with some methyl-cyclohexane and methane). Gas phase: below 180°: nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1254.] With platinum catalyst, or palladium, Zelinsky hydrogenated ethyl-benzene to ethyl-cyclohexane. [*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 274.]

2037A. Polystyrol to hexahydropolystyrol. Polystyrol is dissolved in thiophene-free benzene, nickel catalyst is added and then alcohol. The precipitate of polystyrol and nickel is dried in a vacuum and hydrogenated in a rotary autoclave at 280° C. under 100 atmospheres pressure for two hours. [Staudinger, Geiger and Huber, *Ber.*, 1929, **62**, 263.]

2038. Methyl-ethyl-1, 2-cyclohexene to methyl-ethyl-1, 2-cyclohexane. Gas phase : below 180° : nickel catalyst. [Sabatier: *Catalysis*, 475.]

2039. Pseudocumene (1, 3, 4-trimethyl-benzene) to 1, 3, 4-trimethyl-cyclohexane. Gas phase : 180° (below 250°) : nickel catalyst. Unchanged pseudocumene may be removed by shaking with a mixture of 1 volume fuming nitric acid to 2 volumes concentrated sulphuric acid, a reagent which is almost without effect on the saturated hydrocarbon in the cold. [Sabatier and Senderens, *Compt. rend.*, 1901, 132, 568.]

2040. Mesitylene, 1, 3, 5-trimethyl-benzene to 1, 3, 5-trimethyl-cyclohexane. Gas phase : about 180° (below 250°) : nickel catalyst : almost quantitative : traces of residual mesitylene can be removed by shaking with nitric and sulphuric acid mixture, which is without effect on the saturated hydrocarbon, in the cold. [Sabatier and Senderens, *Compt. rend.*, 1901, 132, 568.]

2041. Butyl-benzene to butyl-cyclohexane (with products of shortening of the side chain). Gas phase : not above 180° : nickel catalyst. [Sabatier: *Catalysis*, 448.] With platinum-black catalyst, butyl-benzene in acetic acid solution yields butyl-cyclohexane. [Halse, *J. prakt. Chem.*, 1915 (2), 92, 40.]

2042. *p*-Cymene (*p*-methyl-isopropyl-benzene), in the gas phase, over nickel, at 180° , gives *p*-methyl-isopropyl-cyclohexane (75 per cent), *p*-dimethyl and *p*-methyl-ethyl-cyclohexane (12½ per cent of each). [Sabatier and Senderens, *Compt. rend.*, 1901, 132, 568 and 1254.]

2043. Durene to hexahydrodurene. Acetic acid solution : platinum-black catalyst. [Willstätter and Hutt, *Ber.*, 1912, 45, 1471.]

2044. Amyl-benzene to amyl-cyclohexane. Liquid phase (acetic acid solution) : platinum-black catalyst. [Halse, *J. prakt. Chem.*, 1915 (2), 92, 40.] The preparation of a large number of homologs is described in this article.

2045. Hexyl-benzene to hexyl-cyclohexane. Liquid phase, acetic acid solution : platinum-black catalyst. [Halse, *J. prakt. Chem.*, (2), 1915, 92, 40.]

2046. Octyl-benzene to octyl-cyclohexane. Acetic acid solution : platinum-black catalyst. [Halse, *J. prakt. Chem.*, 1915 (2), 92, 40.]

2047. Pentadecyl-benzene to pentadecyl-cyclohexane. In acetic acid solution : platinum-black catalyst. [Halse, *J. prakt. Chem.*, 1915 (2), 92, 40.]

2048. Diphenyl may be hydrogenated completely to dicyclohexyl (m.p. 4° , b.p. 233°) in the gas phase, by repeated passages over an active nickel at moderate temperatures (about 170°), with a rapid current of hydrogen. Diphenyl boils at 254° , hence the need for the rapid gas current. [Sabatier and Murat, *Compt. rend.*, 1912, 154, 1390; Eijkmann, *Chem. Weekblad*, 1903, 1, 7, *Chem. Centr.*, 1903 (2), 989.]

2049. Dibenzyl (diphenyl-ethane), $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, in the gas phase over nickel at 160° – 170° hydrogenates to 1, 2-dicyclohexylethane, $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot C_6H_{11}$, b.p. 270° . On account of the high boiling-points of the substrate and of the product, the current of hydrogen must be rapid and one passage will not suffice for the transformation. [Sabatier and Murat, *Ann. Chim.*, 1915 (a), 4, 303.] The same hydrogenation is effected by Ipatiev's method, using "nickel oxide" catalyst at 260° , 120 atmospheres. [Ber., 1907, 40, 1286.]

2050. Diphenyl-propanes to dicyclohexyl-propanes : gas phase, rapid current of hydrogen, several passages over very active nickel at 170° . [Sabatier and Murat, *Ann. Chim.*, 1915 (9), 4, 304.]

2051. Diphenyl-butan-2-ones to dicyclohexyl-butan-2-ones. Gas phase, rapid current of hydrogen : 170° : nickel catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915 (9), 4, 305.]

2052. Diphenyl-pentanes (b.p. above 300°) to dicyclohexyl-pentane. Gas phase, rapid current of hydrogen : 165° : nickel catalyst. [Sabatier and Murat, *Ann. Chim.*, 1915 (9), 4, 307.]

2053. Phenyl-cyclohexene (1, 1) to phenyl-cyclohexane and some diphenyl. Gas phase : 220° , nickel catalyst of slight or modified activity. [Sabatier and Murat, *Compt. rend.*, 1912, 154, 1390.]

2054. Fluorene, $\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_4 \\ | \\ \text{CH}_2 \end{array}$ to decahydrofluorene (b.p. 258°). Gas phase : 150° :

nickel catalyst. [Schmidt and Metzger, *Ber.*, 1907, 40, 4566.]

2055. According to Sadikov and Mikhailov,³ "hydrogenation of fluorene in the presence of osmium at 300° and 165 atmospheres original pressure proceeds much more rapidly than in the presence of nickel and gives a small proportion of dodecahydrofluorene in addition to decahydrofluorene, which is the sole product when nickel is used. Addition of cerium dioxide to the osmium catalyst causes an extraordinary enhancement of its activity, the yield of dodecahydrofluorene attaining about 93 per cent at 300° with a maximal pressure of 153 atmospheres. With thorium dioxide in place of cerium dioxide a still greater activation is observed, and dodecahydrofluorene is the sole product. With nickel oxide hydrogenation proceeds slowly and yields decahydrofluorene and unchanged fluorene; addition of cerium dioxide enormously increases the activity and causes almost exclusive production of dodecahydrofluorene. Thorium dioxide, on the other hand, greatly diminishes the activity of the nickel oxide catalyst."⁴

2056. Cyclohexyl-cyclohexene (1, 1) yields dicyclohexyl on hydrogenation over a slightly active nickel in the gas phase at 220°. [Sabatier and Murat, *Compt. rend.*, 1912, 154, 1390.]

2057. 1-Methyl-6-cyclohexylidene- Δ' -cyclohexene to 1-methyl-2-cyclohexyl-cyclohexane.

2058. 1-Ethyl-6-cyclohexylidene- Δ' -cyclohexene to 1-ethyl-2-cyclohexyl-cyclohexane. 95 per cent ethanol solution : Adams' platinum-black catalyst. [Garland and Reid, *J. Am. Chem. Soc.*, 1925, 47, 2339.]

2059. Triphenyl-methane hydrogenated over nickel at 220° gives dicyclohexyl-phenyl-methane, and at 180° tricyclohexyl-methane. [Godchot, *Compt. rend.*, 1908, 147, 1057.] The second product was obtained by rehydrogenation of the first at 175°-220°.

2060. 1, 10, 10-Triphenylbenzofulvene, $\text{C}_{28}\text{H}_{20}$, to 1-phenyl-3-[diphenyl-methyl]-dihydroindene, $\text{C}_{28}\text{H}_{24}$. Ether (60 cc.) solution : 0.5 g. hydrocarbon, 1.5 g. platinum-black : two hours at atmospheric pressure. With Paal's colloidal palladium hydrogenation failed. [Zalkind (Salkind) and Kruglov, *Ber.*, 1928, 61B, 2311.]

2061. Tetraphenylmethane to dicyclohexylmethane, tricyclohexylmethane and (?) a little phenylcyclohexylmethane. Ipatiev's method : 80-100 atmospheres : 275°-285° : five to six days : nickel catalyst.

2062. Similarly: parahydroxytetraphenylmethane to cyclohexanol, dicyclohexylmethane, tricyclohexylmethane. [Ipatiev and Dolgov, *Bull. Soc. Chim.*, 1927 (iv), 41, 1621; *Brit. Chem. Abst.*, 1928, 163.]

2063. Symmetrical tetraphenylethane to dicyclohexylmethane. Gas phase : 230°-240° : very active nickel catalyst. Sabatier remarks that this hydrogenation has "mis-carried." [Sabatier and Murat, *Compt. rend.*, 1913, 157, 1497.]

2064. Indene to hydrindene. 10 to 15 atmospheres : 200° : nickel catalyst : yield theoretical. [von Braun and Kirschbaum, *Ber.*, 1922, 55 (B), 1680; *J. Chem. Soc.*, 121 and 122 (i), 727.]

2065. Hydrindene, $\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{C}_8\text{H}_7 \\ \diagdown \quad \diagup \\ \text{CH}_3 \end{array}$ to dicyclononane, C_9H_{18} , b.p. 163°. Gas phase : nickel catalyst. [Eijkman, *Chem. Week. Blad.*, 1903, 1, 7, *Chem. Centr.*, 1903 (2), 989.]

³ *Ber.*, 1928, 61B, 1792.

⁴ *Brit. Chem. Abst.*, 1928, 1235A.

NAPHTHALENE, PHENANTHRENE AND ANTHRACENE⁶

2066. Naphthalene to dihydronaphthalene. Liquid phase : nickel catalyst. In a boiling ethyl alcohol solution of naphthalene, the products obtained were invariably mixtures which, however, could be separated readily. The first main product of hydrogenation proved to be 1.4 dihydronaphthalene, and this appears to be the first instance of the preparation of a dihydro derivative in the naphthalene series by direct hydrogenation in presence of a catalyst. A more prolonged reaction, or treatment of 1.4 dihydronaphthalene in boiling ethyl alcoholic solution, led to the formation of some tetrahydronaphthalene, together with a mixture of lower boiling liquids, which were not examined closely, but were probably the more saturated derivatives. [Rowe, *J.S.C.I.*, 1920, 244T. This is a long and important article dealing with the hydrogenation of naphthalene and its compounds. The greater part is taken up with hydrogenation by means of sodium. An article by Rowe and Tarbett, in *J. Soc. Dyers and Col.*, 1925, 41, 5, *Brit. Chem. Abst.*, 1925, 44, 165B, deals with the properties of azo dyes from intermediates obtained by the hydrogenation of naphthalene derivatives.]

2067. Naphthalene to tetrahydronaphthalene, b.p. 205°–207°. Gas phase : 200° : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, 132, 1257.] Vapor carried by the hydrogen current over the catalyst.

2068. Naphthalene to decahydronaphthalene, 189°–191°. Gas phase : 175° : nickel catalyst. [Leroux, *Compt. rend.*, 1904, 139, 672.] Decahydronaphthalene is also formed, in acetic acid solution, by hydrogenation with colloidal palladium catalyst. [Skita, *Ber.*, 1912, 45, 3312.]

2069. By Ipatiev's method, naphthalene is hydrogenated successively to tetrahydro- and to decahydronaphthalene, using the "nickel oxide" catalyst at 250° under 120 atmospheres. [Ipatiev, *Russ. Phys. Chem. Soc.*, 1907, 39, 693; *Chem. Abst.*, 1907, 1, 2877; *Ber.*, 1907, 40, 1281.]

2070. With platinum-black catalyst naphthalene in glacial acetic acid is hydrogenated successively to dihydro-, tetrahydro-, and decahydronaphthalene. [Willstätter and Hatt, *Ber.*, 1912, 45, 1471; Willstätter and King, *Ibid.*, 1913, 46, 527.]

2071. Naphthalene to decahydronaphthalene (decalin). According to Hücker all preparations of decahydronaphthalene are mixtures of the *cis*- and *trans*-forms, the product obtained by the use of platinum-black containing about 90 per cent of the *cis*- and 10 per cent of the *trans*-form. Willstätter and Seitz have examined various preparations made with the aid of platinum and found all to have the constants of the pure *cis*-form, nor could any trace of the *trans*-form be obtained on fractional distillation. Reduction of naphthalene with nickel and hydrogen at 160°–162°, however, yielded chiefly the *trans*-form, d_4^{20} 0.8784; n_D^{20} 1.4729. [Willstätter and Seitz, *Ber.*, 1924, 57B, 683.]⁶

2072. Acenaphthene $C_{12}H_{10}$ to tetrahydroacenaphthene (b.p. 254°), gas phase, 210° and 250°, nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, 132, 1257. Godchot, *Bull. Soc. Chim.*, 1908 (4), 3, 529.]

2073. Acenaphthene to tetrahydroacenaphthene. 10 to 15 atmospheres : 210° : nickel catalyst : yield quantitative. [Von Braun and Kirschbaum, *Ber.*, 1922, 55 (B), 1680; *J. Chem. Soc.*, 121 and 122 (i), 727.]

2074. Hydrogenation of thionaphthene. [Fricke and Spilker, *Ber.*, 1926, 59B, 349.]

2075. Phenanthrene. The results obtained by hydrogenating phenanthrene vapors over nickel vary with the temperature and, seemingly, with other conditions, for the reports of different workers, are conflicting. Working at a little below 200°, with a nickel of high activity, Breteau [*Compt. rend.*, 1905, 140, 942] obtained a mixture of

⁶ For industrial hydrogenation of these hydrocarbons consult Chapters XLI and XLII.

⁷ *J. Chem. Soc. Abst.*, 1924, i, 628.

hexahydrophenanthrene, b.p. 305°, and octohydrophenanthrene, b.p. 280°. Schmidt and Metzger [*Ber.*, 1907, **40**, 4240] at 150° got no farther than the dihydrophenanthrene, while Padoa and Fabris [*Gaz. Chim. Ital.*, 1909, 39 (1), 333] at 200° obtained a mixture of solid dihydrophenanthrene and liquid tetrahydrophenanthrene. By operating at 175° these last workers got dodecahydrophenanthrene. [Sabatier: *Catalysis*, **484**.]

2076. Ipatiev's method, with "nickel oxide" catalyst, at 400° yields in succession dihydro-, tetrahydro-, octohydro-, and perhydrophenanthrene. [Ipatiev, Jakovlev and Rakitin, *Ber.*, 1908, **41**, 996.]

2077. In the presence of palladium sponge, at 150°–160°, phenanthrene vapors, driven by a current of hydrogen, give a mixture of tetra- and octohydrophenanthrene. [Sabatier, **536**.]

2078. Hydrogenation of phenanthrene. See Schroeter, 1924, *Ber.*, **57B**, 2025; *C. A.*, 1925, **19**, 1274.

2079. Phenanthrene : Hydrogenation and Dissociation. Phenanthrene to dihydrophenanthrene, alkyl-naphthalenes, naphthalene and dissociation products of naphthalene. Ipatiev's method, alumina catalyst with copper, nickel, or iron oxide. The temperature of dissociation is about 500° C. with an initial hydrogen pressure of 75 atmospheres. The dissociation products of naphthalene are di-substituted benzenes, containing but little benzene. Dissociation occurs therefore with intermediate production of dihydrophenanthrene and fission of one ring with the formation of naphthalene and alkyl-naphthalenes, the process representing the converse of the synthesis of phenanthrene from naphthalene and ethylene. The second possible mode of dissociation, into diphenyl and ethylene, does not appear to be realized in these experiments, as indicated by the almost complete absence of benzene and toluene from the products. Probably the dissociation of phenanthrene into naphthalene is caused by its tendency to isomerize to the symmetrical anthracene, a process which would be interrupted in its initial stages by the hydrogen and thus give rise to alkyl-naphthalenes. [Orlov, *Ber.*, 1927, **60B**, 1950].¹

2080. Phenanthrene to symmetrical octahydrophenanthrene. [Schroeter, with van Hulle and Müller, *Ber.*, 1924, **57B**, 2025.]

2081. With palladium-black (half the weight of substrate) phenanthrene in cyclohexane solution is hydrogenated to tetrahydrophenanthrene. [Breteau, *Div. méth. hydrog.*, Paris, 1911, 26.]

2082. With platinum-black phenanthrene in cyclohexane solution is not hydrogenated. [Breteau, *loc. cit.*, p. 20.] But in ether solution, in two days at room temperature, in eight hours at the boiling-point of the solution, dihydrophenanthrene was obtained by Schmidt and Fischer [*Ber.*, 1908, **41**, 4252.].

2083. Anthracene. Successive hydrogenations. Gas phase: nickel catalyst. At 260° gives tetrahydroanthracene, $C_{14}H_{14}$, m.p. 89°. At 200°–205° octahydroanthracene, m.p. 71°. By the use of extremely active nickel with slow hydrogen current at 175°–180° the octohydroanthracene may be hydrogenated to perhydroanthracene, $C_{14}H_{14}$, m.p. 88°. [Godchot, *Ann. Chim. Phys.*, 1907 (8), **12**, 468.]

2084. Using Ipatiev's method, at 260°–270°, 100 to 125 atmospheres, for ten to sixteen hours, with "nickel oxide" catalyst, the same successive hydrogenations of anthracene were obtained, with partial destruction of the anthracene. [Ipatiev, Jakovlev and Ratikin, *Ber.*, 1908, **41**, 996.]

2085. Anthracene hydrogenated in the presence of nickel-fuller's earth catalyst, under 10–20 atmospheres pressure at 120°–150° yields, primarily, 9 : 10-dihydroanthracene, then 1 : 2 : 3 : 4-tetrahydroanthracene and symmetrical-octahydroanthracene. (Note the surprising wandering of the hydrogen atoms from positions 9 and 10.) [Schroeter, with Gluschke, van Hulle and Götzky, *Ber.*, 1924, **57B**, 2003.]

¹ *Brit. Chem. Abst.*, **1927**, 1060A.

2086. Hydrogenation of anthracene. See Schroeter, *Ber.*, 1924, **57B**, 2003; *Chem. Abst.*, 1925, **19**, 1271.

2087. Cyclic hydrocarbons such as benzene and its homologs, naphthalene, phenanthrene and anthracene are produced by subjecting aliphatic or hydroaromatic hydrocarbons to the action of hydrogen or hydrogen-containing gases, under pressure, at 500° C., with the use of catalysts. For details the original should be consulted.*

* Brit. Pat., 281,298, Nov. 24, 1926, to I. G. Farbenind. A.-G.

CHAPTER XXI

NUCLEAR HYDROGENATIONS IN SIX-MEMBERED RINGS

HYDROXY COMPOUNDS

2100. Phenol to Cyclohexanol. In the gas phase at 180°, with a nickel catalyst, the product first obtained contains unchanged phenol, also some cyclohexanone and cyclohexene. By separating the fraction boiling 155°–165° and subjecting it to a second passage (with hydrogen) over the nickel at 150°–170°, the phenol and cyclohexanone are completely converted into cyclohexanol. [Sabatier and Senderens, *Compt. rend.*, 1903, 137, 1025.]¹

2101. In the liquid phase, with a nickel catalyst, under 15 atmospheres pressure of hydrogen, at 100°–150°, phenol is rapidly and completely converted into cyclohexanol. [Sabatier: *Catalysis*. 603.]

2102. Phenol can also be hydrogenated to cyclohexanol by use of a platinum-black catalyst. [Willstätter and Hatt, *Ber.*, 45, 1471.]

2103. Brochet² produces alcohols from aldehydes, ketones and phenols by catalytic hydrogenation in the liquid phase (if necessary, by fusion or solution of a solid) or in a suspension of a solid. The catalyst is one of the group with atomic weight between 55 and 59 (iron, nickel, cobalt) with or without a promoter. Brochet prefers to use a moderate plus pressure of hydrogen. The temperature does not exceed 200° C. Vigorous agitation is desirable. *Example:* cyclohexanol from phenol.

2104. Phenol to cyclohexanol. Liquid phase at 190°–215° C. under 25 atmospheres hydrogen pressure: catalyst, mixed oxides of nickel, cobalt and copper.³

2105. Phenol to cyclohexanol, with Adams' platinum oxide catalyst. Phenol 62 g., ethyl alcohol (95 per cent) 50 cc., catalyst 0.65 g.: initial pressure 2.75 atmospheres: time, six and one-half hours: yield 54 g. pure cyclohexanol. For an improved method see under Benzaldehyde. [Voorhees with Adams, *J. Am. Chem. Soc.*, 1922, 44, 1404.]

2106. Anisol to methoxy-cyclohexane. Gas phase: below 150°: nickel catalyst. [Brunel, *Ann. Chim. Phys.*, 1905 (8), 6, 205; Sabatier and Senderens, *Bull. Soc. Chim.*, 1905 (3), 33, 616.] In this reaction there are produced small quantities of cyclohexane and of methanol. Above 300° the hydrogenation of the aromatic nucleus is suppressed, as usual, and the molecule is split, yielding methane, phenol, benzene, methanol.



[Sabatier and Senderens, *Bull. Soc. Chim.*, 1905 (3), 33, 616; Mailhe and Murat, *Bull. Soc. Chim.*, 1912 (4), 11, 122.]

2107. Cinnamic alcohol to cyclohexylpropanol. No solvent: platinum-black catalyst: quantitative yield. [Waser, *Helv. Chim. Acta*, 1925, 8, 117.]

¹ The higher the temperature the larger the yield of cyclohexanone. If the mixed product obtained by operating at 220°–230° C. is passed over a dehydrogenating catalyst (such as copper at 300° C.), practically pure cyclohexanone is obtained.

² U. S. Pat. 1,247,629, Nov. 27, 1917.

³ Ger. Pat. 444,665, Jan. 19, 1919, to Riedel.

2108. Cresols. *o*-Cresol over nickel at 200°–220° gives *o*-methyl-cyclo-hexanol (90 per cent yield), with a small amount of ketone, which can be removed as the sodium bisulphite compound.

2109. *m*-Cresol, in the same conditions, gives a mixture of the alcohol and ketone. On hydrogenating this mixture at 180° the product is almost pure *m*-methyl-cyclo-hexanol.

2110. *p*-Cresol at 200°–230° hydrogenates readily to *p*-methyl-cyclohexanol, with a trace of the ketone. [Sabatier and Mailhe, *Compt. rend.*, 1905, **140**, 350.]

2111. Godchot and Bedos [*Compt. rend.*, 1922, **174**, 461; *Bull. Soc. Chim.*, 1925, **37**, 1451], showed that the product of Sabatier and Mailhe differed from that obtained by the action of magnesium methyl iodide on cyclohexene oxide.

2112. For the isomerism of the methylcyclohexanols prepared by different methods see Gough, Hunter and Kenyon, *J. Chem. Soc.*, 1926, **129**, 2052.]

2113. Adipic esters are obtained from hydrogenated cresols by oxidation and esterification.⁴

2114. Xylenols (dimethyl-phenols) vary in their amenability to hydrogenation. 1, 3-Dimethyl-phenol (4) over nickel at 190°–200°, gives an excellent yield of 1, 3-dimethyl-cyclohexanol (4), with a little ketone and some meta-dimethyl-benzene.

2115. 1, 4-Dimethyl-phenol (2), in the same conditions, yields 10 per cent of ketone, otherwise it hydrogenates regularly to 1, 4-dimethyl-cyclohexanol. But, on the contrary, the principal product of the hydrogenation, in the stated conditions, of 1,2-dimethyl-phenol (4) is ortho-dimethyl-benzene (67 per cent), only 25 per cent is the cyclohexanol, and there is 8 per cent of ketone. [Sabatier and Mailhe, *Compt. rend.*, 1906, **142**, 553.]

2116. Xylenol (*symm*-meta-) to dimethylcyclohexanol. In neutral solution : nickel catalyst. [v. Braun and Haensel, *Ber.*, 1926, **59B**, 1999; *Chem. Abst.*, 1927, **21**, 230.]

2117. Diethyl-phenol to diethyl-cyclohexanol. Gas phase : below 160° : active nickel catalyst. [Henderson and Boyd, *J. Chem. Soc.*, 1911, **99**, 2159.]

2117A. Paraisopropylphenol is easily hydrogenated in presence of nickel at 150° C. to paraisopropylcyclohexanol. [von Braun and Werner, *Ber.*, 1929, **62B**, 1050.]

2118. Hydrogenation of Phenols to Enol Forms.⁵ Catalytic hydrogenation of phenol in cyclohexanol solution with nickel catalyst yields only the enol form of cyclohexanone. (Note.—The possibility of formation of cyclohexanone from the solvent by dehydrogenation was eliminated by the temperature control). Similarly were obtained the enol of paramethyl-cyclohexanone and of carvomenthone.

2119. It appears that reduction of phenols occurs by addition of hydrogen at the two double linkages not contiguous to the hydroxyl group. The resulting enol then ketonizes or is reduced to the secondary alcohol.

2120. Grignard and Mingasson standardize their procedure, using pumice-supported nickel (from the hydroxide) at 280°–300° and cyclohexanol as the solvent for the phenol. For each pressure studied, there is a critical temperature at which cyclohexanol is dehydrogenated to cyclohexanone: 18–22 mm., 155°, and 760 mm., 180°. It is indicated that the non-contiguous double linkages are first hydrogenated to give the enol of the corresponding cyclohexanone. This enol is tautomerized when it is isolated but takes up hydrogen to give cyclohexanol when the hydrogenation is prolonged. If the hydrogenation is carried out at a temperature higher than the critical temperature, cyclohexanone is obtained by secondary decomposition.⁶

2121. Anisol to methoxycyclohexane with some methanol and cyclohexane. Gas phase : below 150° : nickel catalyst. [Brunel, *Ann. Chim. Phys.*, 1905 (8), **6**, 205; Sabatier and Senderens, *Bull. Soc. Chim.*, 1905 (3), **33**, 616.]

⁴ U. S. Pat. 1,643,619, Sept. 27, 1927, to Claassen. Cf. French Pat. 32,991, Feb. 4, 1927 (addition to 611,624) to same patentee; Ger. Pat. 473,960, Feb. 13, 1926 to Deutsche Hydrierwerke A.-G.

⁵ Grignard and Mingasson, *Compt. rend.*, 1927, **185**, 1552; *Brit. Chem. Abst.*, **1928**, 178A.

⁶ *Chem. Abst.*, 1928, **22**, 948.

2121A. Waser, Sommer, Landweer and Gaza (*Helv. Chim. Acta*, 1929, **12**, 418; *Brit. Chem. Abst.*, 1929, 691A), hydrogenated phenol and naphthol ethers in acetic acid solution in presence of platinum black. With phenol ethers there occurred a one-third conversion to the cyclohexyl derivative, $C_6H_{11} \cdot OR$. Other products were the hydrocarbon $R \cdot H$ and cyclohexanol, the phenol $R \cdot OH$ and cyclohexane. Cyclohexanone was an intermediate product.

2122. By Ipatiev's method at 240° and 100 atmospheres, anisol is converted into hexahydroanisol (40 per cent) and some cyclohexanol and cyclohexane. [Ipatiev and Lougovoy, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 470.]

2123. Alkyl-isopropylene phenols to alkyl-isopropyl phenols or the corresponding cyclohexanols. Liquid phase: high pressure and temperature.⁷ By this method are obtained thymol and menthol from 3-methyl-6-isopropylene phenol.

2124. Ortho-allylphenol to ortho-propyl-phenol. Acetic acid solution: platinum catalyst. On protracted hydrogenation one gets a mixture of 2-propylcyclohexanols (mostly the *cis*-form) with about 25-30 per cent propylcyclohexane, 2-propylcyclohexanone is an intermediate stage (as shown by hydrogenation of the latter as starting material). Propylcyclohexanone oxime in aqueous hydrochloric acid, with platinum-black is hydrogenated to 2-propylcyclohexyl- β -hydroxyl-amine: the semi-carbazone yields 2-propylcyclohexylsemicarbazide. For the bearing of these observations on the problem of steric hindrance the original article and the others of the series should be consulted. [Vavon and Anziana, *Bull. Soc. Chim.* 1927 (iv), **41**, 1638; *Brit. Chem. Abst.*, 1928, 166A.]

2125. Acetone and meta-cresol (condensation product) to thymol and stereoisomeric menthols. Acetone and para-cresol (condensation product) to 4-methyl-6-isopropylcyclohexanols. Nickel catalyst: $280^\circ C$: hydrogen under pressure.⁸

2126. The etheric condensation products of an alkylated phenol with a phenol hydrogenated at a higher temperature than usual until 4 or 16 hydrogen atoms are taken up. This is a generalized statement of the hydrogenations described in the foregoing paragraph.⁹

2127. Another proposal¹⁰ involves: (1) preparation of thymol, menthol or isomers by hydrogenating dimethylcoumarane at $250^\circ C$. in presence of carbonates of nickel, cobalt and copper; (2) the production of isopropyl-naphthol, naphthol, isopropyl-naphthalene and naphthalene by hydrogenation of the condensation product of α -naphthol with acetone at 280° - $320^\circ C$., in presence of nickel catalyst.

2128. Directive Modification of Catalysts for Hydrogenation of Alkylated Phenols.¹¹ Catalytic hydrogenation of the condensation products of ketones with phenols yields alkylated phenols or cyclohexanols according to the activity of the catalyst, which may be adjusted by the addition of bismuth for retardation or of manganese for activation. 4:4'-Dihydroxy- $\beta\beta$ -diphenylpropane, treated with hydrogen at 10-20 atmospheres in presence of nickel catalyst containing 3-10 per cent bismuth at 160° , yields *p*-hydroxycumene and phenol. Similarly the product from *o*-cresol and acetone yields 6-hydroxy-*m*-cymene and *o*-cresol. With a nickel catalyst containing 1-8 per cent manganese the corresponding cyclohexanols are obtained.¹²

2128A. 1:2:3:4-Tetrahydrodiphenylene oxide, on hydrogenation in presence of a platinum-palladium catalyst, yields hexahydrodiphenylene oxide. [Ebel, *Helv. Chim. Acta*, 1929, **12**, 3; *Brit. Chem. Abst.*, 1929, 450A.]

⁷ Brit. Pat. application 273,685, convention date June 29, 1926, by Chem. Fabr. auf Akt., vorm. E. Schering; *Chem. Age* (London), 1927, **17**, 222.

⁸ Brit. Pat. application 280,924, convention date Nov. 16, 1926 (addition to 276,010), to Schering-Kahlbaum, A.-G.; *Chem. Age* (London), 1928, **18**, 85.

⁹ Brit. Pat. application 280,956, cond. date Nov. 22, 1926, to Schering-Kahlbaum, A.-G.; *Chem. Age* (London), 1928, **18**, 85.

¹⁰ Brit. Pat. application 293,001, convention date June 29, 1927, to the same patentees.

¹¹ Brit. Pat. 254,753, July 5, 1926 to Chem. Fabr. auf Aktienvorm. E. Schering.

¹² *Brit. Chem. Abst.*, 1928, 740B.

2129. Resorcin (meta-dioxybenzene, phenodiol (1, 3)) in the gas phase at 200°, over nickel, gives phenol and benzene with some cyclohexanol and cyclohexane, but no appreciable amount of cyclohexadiol (1, 3). [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), 4, 428.] Even at lower temperatures (130°) the regular hydrogenation is difficult, on account of the slight volatility of resorcin. Nevertheless, by operating at 130°, small amounts of hexadiol (1, 3), m.p. 65°, have been obtained. [Sabatier and Mailhe, *Compt. rend.*, 1908, 146, 1193.]

2130. 1-Alkyl-dihydroresorcinols to 1-alkyl-cyclohexanones (3). Acetone or alcohol solution: palladium on charcoal catalyst. Thus isopropyl-dihydroresorcinol to 1-isopropyl-cyclohexanone (3).¹³

2131. Resorcinol monoisoamyl ether to 3-hydroxycyclohexyl isoamyl ether. Sabatier's method. [von Braun, Haensel and Zobel, *Ann.*, 1928, 462, 283.]

2132. Guaiacol, pyrocatechin-methyl-ether, hydrogenated by Ipatiev's method, with "nickel oxide" catalyst, at 220°–240° and 100 atmospheres, gives hexahydroguaiacol with some cyclohexanol and cyclohexane. [Ipatiev and Lougovoy, *J. Russ. Phys. Chem. Soc.*, 1914, 46, 470.]

2133. Pyrogallol [benzene-triol (1, 2, 3)] to cyclohexatriol (1, 2, 3), m.p. 67°. Gas phase in brisk current of hydrogen: 120°–130°: active nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1908, 146, 1193.]

2134. In general, the production of the corresponding cyclic compound (polyhydroxycyclohexanes) from polyphenols by catalytic hydrogenation is difficult. At high temperatures the principal products are benzene and phenol, with some cyclohexanol and cyclohexane. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 429.]

2135. Carvacrol to hexahydrocarvacrol. Gas phase: 195°–200°: nickel catalyst. [Brunel, *Compt. rend.*, 1903, 137, 1268.]

2136. Hexahydroxybenzene to inositol (m.p. 218°). Aqueous suspension: 50°–55°: palladium-black catalyst. [Wieland and Wishort, *Ber.*, 1914, 47, 2082.]

2137. α -Ethoxystyrol, $C_6H_5 \cdot C(OC_2H_5) : CH_2$, to α -phenylethyl ethyl ether, $C_6H_5 \cdot CH(OC_2H_5)CH_2$. Absolute ethanol solution: palladium-black.

2138. 1-Methoxy-cyclohexene-1 (cyclohexenyl-methyl ether) to hexahydroanisol (cyclohexyl-methyl ether). Absolute ether solution: palladium-black; carefully dried hydrogen. [Wieland and Garbsch, *Ber.*, 1926, 59B, 2490.]

2139. Phenetol to ethoxy-cyclohexanol. Gas phase: below 150°: nickel catalyst. [Sabatier: *Catalysis*, 464.]

2140. Hydrogenation of unsaturated tertiary alcohols from cyclohexylidene-cyclohexanol, with Voorhees-Adams platinum oxide catalyst. 1-Methyl-2-cyclohexylidene-cyclohexanol to 1-methyl-2-cyclohexyl-cyclohexanol. 1-Ethyl-2-cyclohexylidene-cyclohexanol to 1-ethyl-2-cyclohexyl-cyclohexanol. From the two unsaturated and from the last-mentioned saturated tertiary alcohols, unsaturated hydrocarbons were produced by dehydration by heating with phthalic anhydride. The two hydrocarbons from the unsaturated alcohols were hydrogenated.

2141. 1-Methyl-6-cyclohexylidene- Δ' -cyclohexene gave 1-methyl-2-cyclohexyl-cyclohexane (15.45 g. substrate, 250 cc. alcohol, 1 g. catalyst). 1-ethyl-6-cyclohexylidene- Δ' -cyclohexene gave 1-ethyl-2-cyclohexyl-cyclohexane (12.7 g. substrate, 250 cc. alcohol, 1 g. catalyst). [Garland and Reid, *J. Am. Chem. Soc.*, 1925, 47, 2333.]

2142. 2-cyclohexenylcyclohexanol to a mixture of *cis*- and *trans*-2-cyclohexylcyclohexanols.

2143. 2-cyclohexylcyclohexanone gives the same mixture. [Bedos, *Bull. Soc. Chim.*, 1926 (iv), 39, 473.]

2144. *o-o'*-diphenol to hexahydrodiphenylene oxide. Base metal catalyst (nickel at 225°–230°) with hydrogen under pressure.¹⁴

2145. Hydroxydiphenyls to cyclohexylcyclohexanols. Catalytic perhydrogenation of *p*-hydroxy-diphenyl in presence of platinum-black yields two isomerides identical with

¹³ Seifert, Ger. Pat. 389,851.

¹⁴ Riedel, A.-G., Ger. Pat. 373,850, 1921.

those obtained from *o*-cyclohexylphenol by Schrauth and Görig. Perhydrogenation of *o*-hydroxydiphenyl yields a cyclohexylcyclohexanol having b.p. 172°–177°/75 mm., m.p. 63°. By oxidation a ketone is obtained identical with that obtained by Schrauth and Görig from the oxidation of the above isomerides. [Ranado and Léon, *Anal. Fis. Quím.*, 1924, **22**, 222; *J. Chem. Soc. Abst.*, 1924, i, 849.]

2146. Ortho-hydroxydiphenyl to 2-cyclohexylcyclohexanol (*cis*-form only). Platinum-black catalyst. [Vavon and Mitchovitch, *Compt. rend.*, 1928, **186**, 702; *Brit. Chem. Abst.*, 1928, 516A.]

2147. Parabenzylphenol to 4-benzylcyclohexanol. Under pressure above 200° C. : nickel catalyst. Similarly 4-benzylphenol or 4-benzyl-cyclohexanol to 4-hexahydrobenzylcyclohexanol. [v. Braun, Bayer and Cassel, *Ber.*, 1927, **60B**, 2602.]

2148. 1-Methyl-2-cyclohexylidene-cyclohexanol to 1-methyl-2-cyclohexyl-cyclohexanol. See para. 2140.

2149. 1-Ethyl-2-cyclohexylidene-cyclohexanol to 1-methyl-2-cyclohexyl-cyclohexanol. 95 per cent ethanol : Adams' platinum-black catalyst. [Garland and Reid, *J. Am. Chem. Soc.*, 1925, **47**, 2338.] See para. 2140.

2150. Hydrogenated Dihydroxydiphenylmethane Compounds.¹⁵ 4-Hydroxy-3-methylcyclohexyl-4-hydroxy-3-methylphenyldimethylmethane is obtained from di(4-hydroxy-3-methylphenyl) dimethylmethane, by treatment with hydrogen under pressure at 150°–170° C. in presence of nickel or other hydrogenating catalyst. Other similar hydrogenations are described.¹⁶

2151. *p*-Dihydroxydiphenylmethane to *p*-ethylphenol and phenol. Under pressure : nickel catalyst containing bismuth. With nickel catalyst containing manganese the products are 4-ethylcyclohexanol and cyclohexanol.¹⁷

2152. *p*-Dihydroxydiphenylmethane gives either *p*-cresol and phenol, or 4-methylcyclohexanol and cyclohexanol.¹⁷

2153. *p*-Dihydroxytriphenylmethane gives *p*-benzylphenol and phenol with nickel catalyst containing bismuth.¹⁷

2154. Triphenylcarbinol to tricyclohexylmethane with some dicyclohexylmethane, dicyclohexyl and methane.

2155. 9-Phenylfluorenyl alcohol to perhydro-9-phenyl fluorene. Ipatiev's method at 275° C. [Ipatiev and Dolgov, *Compt. rend.*, 1926, **183**, 304.]

2156. Para-hydroxytriphenylcarbinol to phenol, diphenylmethane, para-hydroxytriphenylmethane. Ipatiev's method : 80–100 atmospheres : 220° : in cyclohexanol : nickel oxide. At 280° the chief product is dicyclohexylmethane, while at 320° some tricyclohexylmethane, methane, are also produced.

2157. Para-hydroxytriphenylmethane at 270°–275° gives tricyclohexylmethane.

2158. Para-hydroxydiphenylmethane at 100 atmospheres and 250°–260° C. gives dicyclohexylmethane. [Ipatiev and Delgov, *Compt. rend.*, 1927, **185**, 1484; *Brit. Chem. Abst.*, 1928, 169A.]

2159. *p*-Hydroxytetraphenylmethane to cyclohexanol, dicyclohexylmethane and phenyldicyclohexylmethane. Ipatiev's method : nickel oxide catalyst : 275°–285° C. : 80–100 atmospheres hydrogen pressure. [Ipatiev and Dolgov, *Compt. rend.*, 1927, **185**, 210.]

2160. Naphthols. α -Naphthol to decahydro- α -naphthol, m.p. 62°, by hydrogenation in the gas phase, over nickel, in two stages, at 170° and at 135°.

2161. β -naphthol, similarly, to decahydro- β -naphthol, m.p. 75°, in two stages, at 170° and then at 150°. [Leroux, *Compt. rend.*, 1905, **141**, 953; *Ann. Chim. Phys.*, 1910, (8), **21**, 483.]

¹⁵ U. S. Pat. 1,593,080, July 20, 1926, to Jordan.

¹⁶ In U. S. Pat. 1,593,081 of same date, to same patentee, description is given of further hydrogenation of these compounds to produce perfume bases.

¹⁷ Brit. Pat. 274,439, July 14, 1926, to Chem. Fab. auf Akt. vorm. E. Schering; *Chem. Abst.*, 1928, **22**, 1982. Cf. para. 1849.

2162. By Ipatiev's method, with "nickel oxide" catalyst, at 250° and 120 atmospheres, the decahydronaphthols are obtained. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 693; *Chem. Abst.*, 1907, **1**, 2877; *Ber.*, 1907, **40**, 1281.]

2163. Beta-naphthol to tetrahydro-beta-naphthol (3 hours) and decahydro-beta-naphthol (5 hours). Liquid phase at 190°–200° C. under 10–30 atmospheres hydrogen pressure: catalyst, mixed carbonates of nickel, cobalt and copper.¹⁸

2164. 4-Cyclohexyl- α -naphthol to 4-cyclohexyldecahydro- α -naphthol. Solution in hexahydrotoluene: 210° C.: 27 atmospheres: nickel: forty minutes. From this by dehydration 1-cyclohexyl- Δ^4 -octahydronaphthalene results, which on hydrogenation at 160° C. and 25 atmospheres yields α -cyclohexyldecahydronaphthalene.

2165. 2-Cyclohexyl- α -naphthol hydrogenated at 180° and 25 atmospheres for thirty minutes yields 2-cyclohexyldecahydro- α -naphthol. Using a regenerated catalyst at 215° C., at 26 atmospheres, for twenty-five minutes, another form, of lower melting-point, is obtained which, after dehydration and re-hydrogenation, gives β -cyclohexyldecahydronaphthalene.

2166. 1-Cyclohexyl- β -naphthol gives β -cyclohexyl decahydronaphthalene. 6-cyclohexyl- β -naphthol gives 6-cyclohexyl decahydro- β -naphthol.

2167. α -Tetrahydro-3-cyclohexyl- β -naphthol hydrogenates to a resin. [Alberti, *Annalen*, 1926, **450**, 304; *Chem. Abst.*, 1927, **21**, 1114.]

2168. 1 : 2 : 3 : 4-Tetrahydronaphthalene-1 : 2-oxide on catalytic reduction yields only tetrahydro- β -naphthol. [Kötz and Hoffmann, *J. prakt. Chem.*, 1925, **110**, (ii), 101.]

KETONIC COMPOUNDS

2169. Acetophenone to ethylcyclohexane. Alcohol, ether, ethyl acetate or acetic acid solution: platinum-black catalyst (with aqueous alcohol methylphenylcarbinol is obtained.) [Vavon, *Compt. rend.*, 1912, **155**, 287.] The same result is obtained in the gas phase at 180° C., with active nickel catalyst. [Sabatier: *Catalysis*, **455**.]

2170. Tetrahydroacetophenone $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ to hexahydro-acetophenone. Gas phase: 160°: nickel catalyst. [Darzens and Rost, *Compt. rend.*, 1910, **151**, 758.]

2171. Cyclohexenone, under 2 atmospheres pressure, with colloidal palladium catalyst, takes up H_2 to form cyclohexanone. [Wallach, *Annalen*, 1904, **336**, 37.]

2172. Dibenzyl-ketone to symmetrical dicyclohexyl-propane. Gas phase: 175°: active nickel catalyst. [Sabatier and Murat, *Compt. rend.*, 1912, **155**, 385.]

2172A. 3 : 5-Diphenylcyclohexenone, with Ipatiev's technique, at 240° C., under 50 atmospheres of hydrogen, with nickel oxide catalyst, yields two isomeric 1 : 3-dicyclohexylcyclohexanes. [Petrov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1441, and *Ber.*, 1929, **62B**, 642; *Brit. Chem. Abst.*, 1929, 316A and 551A.]

2173. Distyryl ketone to di- β -phenylethyl ketone: benzene solution: 170°–180° C.: 70–100 atmospheres: 15 per cent nickel oxide. Maximum yield (60 per cent) was obtained in 15 per cent solution. The yield in alcohol solution is less: in cyclohexane solution the reduction fails. But the product, di- β -phenylethyl ketone, in cyclohexane solution is hydrogenated to α -dicyclohexylpentane. [Ipatiev and Orlov, *Bull. Soc. Chim.*, 1927, **41** (iv), 862.]

2173A. Catalytic reduction of cyclo-pentadienebenzoquinone gives tetrahydro-dicyclopentadienebenzoquinone. [Staudinger, *Ann.*, 1928, **467**, 73.]

2174. Acenaphthenequinone to $\text{C}_{14}\text{H}_{18}\text{O}_4$, a quadrivalent alcohol. In suspension in $\frac{1}{2}$ per cent aqueous sodium hydroxide: (or suspension in ammonia of equivalent strength): colloidal platinum catalyst, with gelatin protective colloid: 3 atmospheres hydrogen pressure: 50° C.: shaking. [Skita, *Ber.*, 1927, **60**, 2525.]

2175. Acenaphthenequinone to $\text{C}_{14}\text{H}_{18}\text{O}_4$. Acid solution: colloidal platinum catalyst. (*Idem*, *Ber.*, 1925, **58**, 2697.) See also: v. Braun and Bayer. Catalytic hydrogenation of acenaphthenequinone under pressure in presence of nickel. *Ber.*, 1926, **59B**,

¹⁸ Ger. Pat. 444,665, Jan. 19, 1919, to Riedel.

920; *Chem. Abst.*, 1926, **20**, 2852. Products were: acenaphthene, tetrahydroacenaphthene, acenaphthenone, acenaphthylene, and acenaphthenol.

2176. Anthraquinone to tetrahydroanthraquinone. Suspension in decalin or tetralin: nickel catalyst: 75° C.: hydrogen pressure 50 atmospheres. [*Skita, Ber.*, 1927, **60**, 2526.] At 90° C. hexahydroanthraquinone is produced. [*Ibid.*] At 150° C. and under 150 atmospheres hydrogen pressure, octahydroanthraquinone results. [*Ibid.*]

2177. Alkylated Anthraquinones. Hydrogenated under Pressure with Nickel Catalyst.¹⁹ 1:4-Dimethylantraquinone in decalin at 180° C. gives 1:4-dimethyl-1:2:3:4-tetrahydroanthranol (and a little 1:4-dimethyl-(?)1:4-dihydroanthranol) The tetrahydroanthranol is hydrogenated further to 1:4-dimethyl-1:2:3:4:5:6:7:8 octahydroanthranol and, finally, to 1:4-dimethyl-1:2:3:4:5:6:7:8 octahydroanthracene.

2178. 1-Methyl-anthraquinone yields (?) 1-methyl-1:2:3:4-tetrahydro-9-anthranol and then 1-methyl-1:2:3:4:5:6:7:8-octahydroanthracene.

2179. 2-Methylantraquinone gives, first (?) a mixture of isomeric 2(3)-methylantranol, then a mixture of 10 per cent 2-methylantranol, of the reduction products of this and of 2 (3)-methyltetrahydroanthranols.

2180. In an earlier paper [*Ber.*, 1926, **59B**, 914] v. Braun and Bayer reported that 1-methyl-anthraquinone in decalin solution, at 150°-170° C., was catalytically reduced to α -methyl-anthrone, with 70 per cent yield.²⁰

2181. Anthraquinone and its derivatives are treated with hydrogen at an elevated temperature and pressure and in presence of a catalyst. In this manner, anthrone, tetrahydroanthranol, octahydroanthranol, 1:4-dimethylantranol, 1:4-dimethyl-tetrahydroanthranol, 1:4-dimethyl-decahydro-anthracene, 2:3-tetramethylene-anthranol, 2:3:6:7-bis-tetramethylene- α -naphthol, tetrahydronaphthacene, β -hydroxy-octahydroanthranol, α -amino- β -methyl-anthraquinone and other compounds can be obtained, the degree of hydrogenation depending on the quantity of hydrogen.²¹

2181A. Benzanthrone treated with hydrogen under pressure, with a nickel catalyst at 120° C., yields tetrahydrobenzanthrone.^{21a} With increase of temperature to 160-200°, four more atoms of hydrogen are taken up, giving C₁₇H₁₈O. Above 200° C. a hydrocarbon C₁₇H₁₈ is eventually obtained.^{21b}

2182. Hydrogenation of phenanthraquinone proceeds similarly to that of anthraquinone, affecting first the quinone complex and subsequently one side nucleus after the other. Differences are found in the possibility of so moderating the reduction of phenanthraquinone that phenanthraquinol in addition to 9-phenanthrol can be isolated, thus clearly establishing the first step in the action. Also, owing to the lower stability of the hydrogenated derivatives of phenanthrene in comparison with those of anthracene, the individual products are obtained in lower yield, and it is not possible to trace the several phases of the change in so quantitative a manner. Phenanthraquinone dissolved in decahydronaphthalene readily absorbs 2 atomic proportions of hydrogen at 160°, yielding 9-phenanthrol and phenanthraquinol. Further hydrogenation occurs only at a much higher temperature and after 8 atomic proportions of hydrogen have been absorbed, gives a mixture of di- and tetra-hydrophenanthrol. This compound is probably a mixture of 2 isomeric forms, although this view is not supported by its definite melting-point and non-separability by solvents. More complete hydrogenation of phenanthraquinone or 9-phenanthrol affords a mixture of octahydrophenanthrene and octahydrophenanthrol.

2183. Technical benzanthrone is readily purified by recrystallization from decahydronaphthalene and in this solvent absorbs 4 atomic proportions of hydrogen at 160°, a

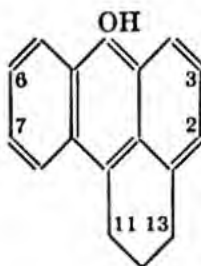
¹⁹ v. Braun, Bayer and Fieser, *Ann.*, 1927, **459**, 287.

²⁰ *Chem. Abst.*, 1926, **20**, 2851.

²¹ Brit. Pat. 248,759, to I. G. Farbenind. A.-G., assignees of J. D. Riedel, A.-G.; convention date, Mar. 3, 1925; *Chem. Age* (London), 1925, **14**, 363.

^{21a} Ger. Pat. 453,578, to Leopold Cassella & Co., G. m. b. H. (Bayer inventor).

^{21b} Ger. Pat. 473,456, Dec. 4, 1925 to the same patentees.



further 4 somewhat more slowly at 200°, and the final 2 at 250°. [von Braun and Bayer, *Ber.*, 1925, 58, 2667; *Brit. Chem. Abstracts*, 1926, 172A. See also *Chem. Abst.*, 1926, 1403.] 1:9-Trimethylene-5:6:7:8-tetrahydroanthracene, is obtained together with 1:9-trimethylene-5:6:7:8-tetrahydroanthracene at 180°–200°; at 250°, the hydrocarbon is practically the sole product of the change, even when the reaction is very prolonged. [In naming these derivatives, it does not appear possible to express the genetic relationship to benzanthrone in any simple manner, and von Braun and Bayer treat them as substituted anthracene derivatives in which the fourth ring is 1:9-trimethylene.]

2184. Phenanthraquinone in the presence of glacial acetic acid, concentrated hydrochloric acid, chloroplatinic acid, colloidal platinum, and water at 50°–60° yields 9:10-dihydroxydecahydrophenanthrene. If the mineral acid is omitted, the reaction terminates with the production of 9:10-dihydroxy-9:10-dihydrophenanthrene.

2185. Anthraquinone in acid solution in the presence of colloidal platinum affords octahydroanthraquinol, m.p. 242°, which is converted by the action of air on its solution in benzene or acetone into octahydroanthraquinone, m.p. 183°. It is remarkable that the hydrogenation of anthraquinone under these conditions does not invariably proceed to the production of the octahydroanthraquinol, but sometimes ceases when tetra- or hexahydroanthraquinol has been produced. The phenomenon appears to depend on the size of the colloidal platinum particles. The isolation of tetrahydroanthraquinol, decomp. (indef.) 206°–216° (acetate, m.p. 204°–206°), is effected with certainty if mineral acid is omitted from the mixture. Certain reduction to the hexahydroanthraquinol stage is effected by careful regulation of the quantities of hydrochloric acid and platinum.

2186. Reduction of 2-methylanthraquinone in the presence of mineral acid affords 2-methyl-1:2:3:4:5:6:7:8-octahydroanthraquinol, m.p. 193°. Similarly, 2-aminoanthraquinone yields 2-amino-octahydroanthraquinol.

2187. Hydrogenation of acenaphthenequinone under the conditions described for anthraquinone proceeds with unusual ease, and if reaction is stopped after the absorption of 10 atomic proportions of hydrogen, gives a mixture of products from which the following compounds are isolated: a dihydroxytetrahydroacenaphthene, hexahydroacenaphthene, $C_{12}H_{14}$, more highly hydrogenated acenaphthenequinones from which individual substances could not be isolated; and a substance, $C_{14}H_{16}O_4$, m.p. 206°. [Skita, *et al.*, *Ber.*, 1925, 58B, 2685.]

2188. Xanthone, Hydrogenation under Pressure with Nickel Catalyst.²³ Xanthone is very rapidly hydrogenated at about 200° mainly to xanthene. Further addition of hydrogen (8 atoms) leads to a mixture of xanthone, xanthene, hexahydroxanthene, and products richer in hydrogen from which a homogeneous material can be isolated with great difficulty. It is therefore preferable to continue the action until all the xanthene

has been reduced; hexahydroxanthene, $C_6H_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \end{array} C_6H_4$, and (?) tetrahydroxanthene,

are then readily isolated. Further hydrogenation at 220°–230° affords dodecahydroxanthene, and *o*-hexahydrobenzylcyclohexanol, which may be a mixture of *cis*- and *trans*-isomerides. Still further hydrogenation increases the yield of *o*-hexahydrobenzylcyclohexanol, but causes also production of dodecahydrodiphenylmethane.²⁴

2189. Preparation of Hydrogenated Polynuclear Quinones. Polynuclear quinones and their derivatives are catalytically hydrogenated, and the resulting nuclear-hydrogenated quinols (glycols) are oxidized.²⁵

²³ *Brit. Chem. Abst.*, 1926, 173A.

²⁴ von Braun and Bayer, *Ber.*, 1926, 59B, 2317.

²⁵ *Brit. Chem. Abst.*, 1926, 1253A. Cf. para., 1977.

²⁶ French Pat., to Skita, 594,291, Mar. 2, 1925; *Brit. Chem. Abst.*, 1927, 398B.

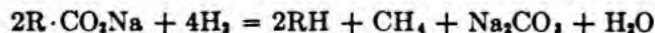
CHAPTER XXII

NUCLEAR HYDROGENATION IN SIX-MEMBERED RINGS

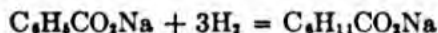
ACIDS, SALTS AND ESTERS

2200. Benzoic Acid. Hydrogenated by Ipatiev's method alkali benzoates give hexahydrobenzoate. E.g., potassium benzoate at 280°, with nickel oxide catalyst, in nine hours gives 40 per cent of potassium hexahydrobenzoate. Sodium benzoate is even more readily hydrogenated. Reaction goes better in two stages: Yield, 60 per cent. [Ipatiev and Philipev, *Ber.*, 1908, **41**, 1001.]

2201. Sodium, potassium, lithium, calcium, and barium benzoates are converted into the corresponding hexahydrobenzoates when mixed dry with nickel oxide and heated under high pressure in an atmosphere of hydrogen at 275°–300°. Under similar conditions, zinc, nickel, and ferrous benzoates undergo profound change, yielding gaseous products containing much methane and carbon dioxide and an intensely red sublimate which has not been investigated fully. Sodium salicylate is very readily hydrogenated, with loss of the carboxyl group and formation mainly of cyclohexanol; salicylic and *p*-hydroxybenzoic acids are much more slowly reduced, giving homogeneous cyclohexanol unaccompanied by cyclohexanone. Mandelic acid is not hydrogenated, owing to the ease with which it yields resinous compounds, whereas sodium mandelate loses its aliphatic hydroxyl group and becomes converted into phenylacetic acid, which suffers partial reduction to cyclohexylacetic acid.¹ [Ipatiev and Rasuvajev, *Ber.*, 1926, **59**, 306 (*cf. Ibid.*, 2028; *Brit. Chem. Abst.*, 1926, 1138A); *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 122.] The work reported in the later paper showed that the reactions:



and



are more complete in the presence than in the absence of water.

2202. With colloidal palladium, under 2 atmospheres pressure, benzoic acid, in acetic acid solution, is hydrogenated to hexahydrobenzoic acid. [Skita and Meyer, *Ber.*, 1912, **45**, 3589.]

2203. Benzoic acid (ethyl ester) to hexahydrobenzoic acid (ethyl ester) with Voorhees-Adams platinum oxide catalyst: 2–3 atmospheres pressure: ethyl benzoate 100, ethyl alcohol (95 per cent), 120 cc., 0.4 to 0.5 catalyst: forty-eight hours. [Grey and Marvel, *J. Am. Chem. Soc.*, 1925, **47**, 2799.]

2204. Sodium benzoate in ethyl alcohol (95 per cent in the presence of platinum-black gives not only sodium hexahydrobenzoate (66 per cent yield) but also ethyl hexahydrobenzoate (33 per cent). In butyl alcohol also some, though much less, esterification takes place. [Waser, *Helv. Chim. Acta*, 1925, **8**, 117.]

2205. Methyl benzoate can be hydrogenated satisfactorily to methyl-cyclohexanol-carboxylate, by hydrogenation of its vapor over nickel, "at a perfectly regulated temperature below 170° C." [Sabatier and Murat, *Compt. rend.*, 1912, **154**, 924.]

¹ *Brit. Chem. Abst.*, 1926, 400A.

2206. Esters of Aromatic Carboxylic Acids: Hydrogenation.² Ring hydrogenation of these esters is effected at moderate hydrogen pressures (25–40 atmospheres) in presence of a nickel catalyst (with or without cobalt) and with or without a solvent. Acids derived from naphthalene take on hydrogen only at the unsaturated parts of the nucleus. *Examples:* ethyl benzoate to ethyl hexahydrobenzoate; ethyl phenylacetate to ethyl hexahydrophenylacetate; methyl salicylate to methyl hexahydrosalicylate; diethyl phthalate to diethyl hexahydrophthalate; dimethyl terephthalate to dimethyl hexahydroterephthalate; ethyl α -naphthoate to ethyl 5, 6, 7, 8-tetrahydro-1-naphthoate; ethyl 2, 3-amino-naphthoate to ethyl 5, 6, 7, 8-tetrahydro-2, 3-amino-naphthoate.

2207. Catalytic Reduction of Hydroxybenzoic Acids. Reduction of aqueous salicylic acid by hydrogen and colloidal platinum at 60° yields finally cyclohexanol in 50 per cent yield. Similarly, *m*- and *p*-hydroxybenzoic acids yield hexahydro-*m*- and *p*-hydroxybenzoic acids, respectively.³

2208. Salicylic acid, ortho-hydroxybenzoic acid, to hexahydrosalicylic acid. Platinum oxide catalyst. [Aguirreche, *Anales soc. españ. fis. quim.*, 1927, **25**, 313.]

2209. Hydroxybenzoic acid in acetic acid solution, with platinum-black catalyst is hydrogenated to hydroxycyclohexane carboxylic acid. [Houben and Pfau, *Ber.*, 1916, **49**, 2294.]

2210. 1, 2-Cyclohexanol carboxylic acid to 1, 2-tetralsalicylic acid. Acetic acid solution: platinum sponge catalyst: fourteen days: with colloidal platinum, Skita method, in seventy-five minutes. γ -o-Carboxyphenyl-*n*-butyric acid to γ -o-carboxycyclohexyl-*n*-butyric acid. Acetic acid solution: platinum sponge catalyst.⁴

2211. α -Hydroxy- β -naphthoic acid, γ : 2-C₁₀H₈(OH)COOH, to 1, 2 tetralsalicylic acid. Acetic acid solution: platinum sponge catalyst: fourteen days. With colloidal platinum (Skita method) this reduction takes place in seventy-five minutes.⁴

2212. Tetralsalicylic acid to hydroxydecalincarboxylic acid. Platinum sponge catalyst: three weeks.⁴

2213. Ethyl ester of α -tetralone- β -carboxylic acid to a mixture: Ethyl decalin- β -carboxylates, *cis* and *trans*; α -decalone and a 1-hydroxydecalin-2-carboxylic acid. Glacial acetic acid solution: platinum sponge: three weeks.⁴

2214. γ -o-Carboxyphenyl-*n*-butyric acid to γ -o-carboxycyclohexyl-*n*-butyric acid. Acetic acid solution: platinum sponge catalyst.⁵

2215. 1-Naphthol-2-carboxylic acid gives 1-hydroxy-5:6:7:8-tetrahydronaphthalene-2-carboxylic acid, which hydrogenates further with difficulty to 1-hydroxy-decahydronaphthalene-2-carboxylic acid.⁵

2216. Ethyl ester of 1-keto-1:2:3:4-tetrahydronaphthalene-2-carboxylic acid gives a mixture of ethyl decahydronaphthalene-2-carboxylate and ethyl 1-hydroxydecahydronaphthalene-2-carboxylate.⁵

2217. Meta-hydroxyphenylacetic acid to cyclohexylacetic acid and some 3-hydroxycyclohexylacetolactone. Glacial acetic acid: platinum-black catalyst. [Robinson and Zaki, *J. Chem. Soc.*, 1927, 2411; *Chem. Abst.*, 1928, **22**, 392.]

2218. Hydrocinnamic esters to esters of β -cyclohexyl-propionic acid. Gas phase: 170°–185°: nickel catalyst. [Sabatier and Murat, *Compt. rend.*, 1913, **156**, 751.] The yield was quantitative and the product pure. In this way were prepared the methyl, ethyl, propyl, isobutyl esters.

2218A. Cinnamic acid (sodium salt) to cyclohexylpropionic acid (sodium salt). Ipatiev's method: nickel catalyst: 300°C.: 100 atmospheres. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1414.]

² Brit. Pat. 286,201, Feb. 26, 1927, to I. G. Farbenind. A.-G.; French Pat. 649,626, Feb. 23, 1928, to I. G.; *Chem. Abst.*, 1929, **23**, 2986.

³ Balás and Kosik, *Časopis Českoslov. Lék.*, 1927, **7**, 118, 136, 191; *Chem. Zentr.*, 1928, i, 1173; *Brit. Chem. Abst.*, 1928, 1005A.

⁴ Hüchel and Goth, *Ber.*, 1924, **57B**, 1285.

⁵ Hüchel and Goth, *Ber.*, 1924, **57**, 1285.

2219. Ortho-, meta-, and para-toluic acid (esters) to ortho-, meta-, and para-hexahydrotoluic acid (esters). Gas phase : 180° : nickel catalyst. [Sabatier, *Catalysis*, 471.]

2220. Phenylacetic acid (ethyl ester) to cyclohexyl acetic acid (ethyl ester). Gas phase : 180° : nickel catalyst. [Sabatier and Murat, *Compt. rend.*, 19B, 156, 424.] The yield was quantitative and the product pure. Methyl, propyl, isobutyl, and isoamyl esters were also prepared.

2221. *o*-Phenyleneaceticpropionic acid with Voorhees-Adams platinum oxide catalyst to the hexahydro derivatives (probably a mixture of isomerides). 10 g. acid, 150 cc. ethyl alcohol (95 per cent, 1 g. catalyst, 50°, 2-3 atmospheres. [Hiers and Adams, 1926, *Ber.*, 59B, 162, *Chem. Abst.*, 1926, 20, 1599; cf. *Chem. Abst.*, 1926, 20, 376; Helfer, *Chem. Abst.*, 1924, 18, 270, Skita, *Ber.*, 1924, 57B, 1977, *Chem. Abst.*, 1925, 19, 824.]

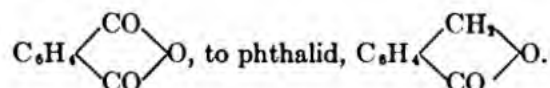
2222. Cyclohexene-acetic acid. The ethyl ester of this acid is converted into ethyl hexa-hydrophenyl-acetate, by hydrogenation in the gas phase over nickel at 160°. [Darzens, *Compt. rend.*, 1907, 144, 328.]

2223. Ethyl 3-isoamyloxycyclohexenylacetate to 3-ethylcyclohexyl isoamyl ether. Methanol solution : platinum or palladium catalyst. [von Braun, Haensel and Zobel, *Ann.*, 1928, 462, 283.]

2224. Phthalic anhydride to hexahydrophthalic acid (low yield) and hexahydrotoluic acid. Platinum oxide catalyst. [Aguirreche, *Anales soc. españ. fis. quim.*, 1927, 25, 313.]

2225. Phthalic acid (potassium salt) to *trans*-hexahydrophthalic acid (potassium salt). Ipatiev's method : 300° : "nickel oxide" catalyst. [Ipatiev and Philipev, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 500; *Ber.*, 41, 1001 (1908)]. Some benzoic acid and methane are formed. The sodium salt gives the hexahydrobenzoate.

2226. Phthalic anhydride,



Gas phase : 200° : nickel catalyst. The second—CO—is not hydrogenated, even at 130°, with very active nickel. [Eijkman, *Chem. Weekblad.*, 1907, 4, 191.]

2227. By Willstätter's method, i.e., platinum-black catalyst aërated, phthalic anhydride is hydrogenated to hexahydrophthalid, ortho-hexahydrotoluic acid and hexahydrophthalic acids. The aëration is essential : isophthalic acid containing a trace of anhydride cannot be hydrogenated with a platinum-black catalyst unless it be aërated. [Willstätter and Jacquet, *Ber.*, 1918, 51, 767.]

2227A. Hydrogenation of monomethyl orthophthalate with platinum-black catalyst gives *cis*-hexahydrophthalate. [Vavon and Peignier, *Bull. Soc. Chim.*, 1929, 45, 293.]

2228. Δ^1 -tetrahydrophthalic anhydride to Δ^2 -tetrahydrophthalide. Vapor phase : nickel catalyst : 220°-240° C. Similarly all phthalic anhydrides reduced partly in the benzene ring will be hydrogenated to phthalides without further hydrogenation in the nucleus. [Mazza and Di Mase, *Gazzetta*, 1927, 57, 300.]

2229. $\Delta^{2,6}$ -Dihydrophthalic anhydride in above conditions gave a 50 per cent yield of $\Delta^{2,6}$ -di-hydrophthalide. [Mazza and Calò, *Ibid.*, 311.]

2230. Δ^1 -tetrahydrophthalic anhydride gave Δ^1 -tetrahydrophthalide. (Mazza and Cremona, *Ibid.*, 318.)^a

2231. 3^c-benzoyl-2^c-phenylcyclopropane-1^c-carboxylic acid to α -phenacyl- β -phenylpropionic acid. Palladized barium sulphate catalyst.

2232. 3^t-benzoyl-2^t-phenylcyclopropane-1^c-carboxylic acid gives the same product. [Stoermer and Schenck, *Ber.*, 1927, 60B, 2566; *Brit. Chem. Abst.*, 1928, 174A.]

^a This work is summarized in: *Atti II congresso naz. chim. pura applicata*, 1926, 1340.

2233. A dimeride, obtained by the vacuum distillation of bis-cinnamylidenemalononic acid when subjected, as the sodium salt, to catalytic hydrogenation gives an acid, m.p. 151° – 152° C., regarded as a hexahydro derivative. [Stobbe, Hensel and Simon, *J. prakt. Chem.* 1925 (ii), 110, 120; *J. Chem. Soc.*, 1925 (i), 1067.]

2234. α - and β -naphthoic acids to dihydronaphthoic acids (eight to nine hours) : tetrahydronaphthoic acids (thirty-two hours) : decahydronaphthoic acid (fifty to sixty hours). Acetic acid (99 per cent solution) : platinum (oxide) black catalyst. [Ranado and Léon. *Anales soc. españ. fis. quim.*, 1927, 25, 421; *Chem. Abst.*, 1928, 22, 777; Léon and Charro, *Ibid.*, 1928, 26, 423; *Chem. Abst.*, 1929, 23, 2172.]

2235. Naphthalic acids (sodium salts) are hydrogenated by Ipatiev's method, using copper catalyst at 300° and 100 atmospheres. The α -acid gives only tetrahydronaphthalene, while the β -acid hydrogenates successively to the tetrahydro-acid. The sodium salt of the β -tetrahydronaphthoic acid, on further hydrogenation gives a mixture of decahydronaphthalene and decahydronaphthoic acid (sodium salt). [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1414; *Ber.*, 1909, 42, 2100.]

2236. Naphthalic anhydrides can be hydrogenated in acetic acid solution, with a platinum-black catalyst, but the catalyst must be aerated from time to time during the operation. The products are: tetrahydronaphthalid, hexahydronaphthalid, decahydroacenaphthene, and tetrahydromethyl (1) naphthalene-carboxylic acid (8). [Willstätter and Jacquet, *Ber.*, 1918, 51, 767.]

2237. Abietic⁷ acid to dihydroabietic acid. Platinum-black catalyst. The iodine value does not decrease with this hydrogenation. This relation also holds between *d*-pimaric acid and dihydropimaric acid. [Johansson, *Arkiv. Kem. Min. Geol.*, 1917, 6 (19); *J.S.C.I.*, 1920, 39, 198A.]

2237A. The same degree of hydrogenation of abietic acid was obtained by Wienhaus [*Z. angew. Chem.*, 1921, 34, 257], by his pupil Lambrecht (*Göttingen Dissertation*, 1920) and by Engelhardt (*Göttingen Dissertation*, 1924), using an abietic acid obtained by vacuum-distillation. They worked in methyl or ethyl alcohol solution with a palladium catalyst.

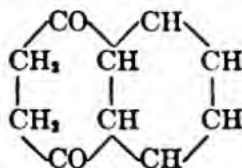
2237B. Ruzicka and Meyer, and Ruzicka and Schinz [*Helv. Chim. Acta*, 1922, 5, 324], were able to hydrogenate an (American) abietic acid to the tetrahydro derivative.

2238. *p*-Aminobenzoic acid to *p*-aminocyclohexane carboxylic acid. Aqueous suspension : platinum-black catalyst. [Houben and Pfau, *Ber.*, 1916, 49, 2294.]

2239. Phenylglycine-*o*-carboxylic acid to hexahydrophenylglycine-*o*-carboxylic acid. Glacial acetic acid solution : Platinum sponge : 50° – 60° : ten to twelve hours. The dimethyl- and diethyl-esters undergo the same hydrogenation. [Vörlander and Kluge, *Ber.*, 1926, 59B, 2075.]

2240. Naphthostyryl (lactone of *peri*-amidonaphthoic acid) (or homolog, or substitution product) to 10 : 3 : 4 : 5-tetrahydronaphthostyryl (or homolog, or substitution product). Liquid phase (solvent); nickel catalyst.⁸

2241. Di-ene Hydrocarbon Addition Compounds. 1 : 4-Endomethylene-5 : 8-diketodecahydronaphthalene results from hydrogenation, in alcoholic solution with colloidal palladium, of



which is the dihydro-derivative of a substance obtained by Albrecht by combining cyclopentadiene with *p*-benzoquinone. [Diels and Alder, *Ann.*, 1928, 460, 98.]

⁷ Abietic acid is a phenanthrene derivative, and is the acid of colophony. For industrial hydrogenation of rosin, etc., consult paragraph 4176 and following paragraphs.

⁸ Brit. Pat. application 281,257, convention date Nov. 25, 1926, to I. G. Farbenind. A.-G.; *Chem. Age* (London), 1928, 18, 103; French Pat. 644,486, Nov. 25, 1927.

2242. Maleic anhydride and cyclopentadiene give *cis*-3 : 6-endomethylene- Δ^4 -tetrahydrophthalic anhydride, the sodium salt of whose acid hydrogenated in presence of palladium gives *cis*-3 : 6-endomethylenecyclohexane-1 : 2-dicarboxylic acid (salt). [*Ibid.*]

2243. Maleic anhydride with butadiene gives *cis*- Δ^4 -tetrahydrophthalic anhydride, whose acid, on hydrogenation, yields *cis*-hexa-hydrophthalic acid. [*Ibid.*]

2244. Cyclopentadiene and acrylic acid unite to form 2 : 5-endomethylene- Δ^1 -tetrahydrobenzoic acid reducible to the corresponding hexahydro-acid. [*Ibid.*]

2245. With acraldehyde cyclopentadiene gives 2 : 5-endomethylene- Δ^1 -tetrahydrobenzaldehyde, which can be hydrogenated to the corresponding hexahydroaldehyde. [*Ibid.*]

2246. Acraldehyde and butadiene give Δ^1 -tetrahydrobenzaldehyde whose semicarbazone is reducible to hexahydrobenzaldehyde semicarbazone. [*Ibid.*]

AMINES

2247. Aromatic amines can be hydrogenated with the Voorhees-Adams platinum oxide catalyst. This catalyst has advantages over Skita's colloidal platinum for these reductions. Complete reductions are obtained with smaller amounts of platinum. The comparative experiments were made on aniline, methyl-aniline, dimethyl-aniline and benzylamine. Traces of ferrous salts poison this reduction catalysis. [Hiers and Adams, *Ber.*, 1926, **59B**, 162; *Chem. Abst.*, **20**, 1599.]

2248. An alkali or an alkaline earth may be added in the catalytic hydrogenation of aromatic bases. *Examples:* ethylaniline with nickel oxide and sodium carbonate; orthotoluidine with cobalt oxide and lime.⁹

2249. Reduction of Aromatic Amines. Substituted aromatic amino compounds are treated with hydrogen under pressure in presence of metal catalysts, such as nickel, cobalt and copper. Examples given are the making of: hexahydroethylaniline; acetyl-*ar*-tetrahydro- α -(or β)-naphthylamine, 2-amino-3-*ar*-tetrahydronaphthoic acid.¹⁰

2250. Production of Hexahydroaniline. Aniline is heated to 250°-300° C. in the presence of cobalt as a catalyst and with a hydrogen pressure of about 100 atmospheres.¹¹

2250A. Lommel and Goost have improved the hydrogenation of aromatic bases, under pressure (*e.g.*, 100 atmospheres) in presence of a catalyst (*e.g.*, nickel) by arresting the reaction, separating the hydrogenated product by distillation, and resuming the hydrogenation of the unchanged portion.^{11a}

2250B. The same workers hydrogenate the homologs of aniline at high temperatures and pressures, using a catalyst containing a substance of the group comprising copper, metals of the platinum and iron groups, and oxides and salts of these metals.^{11b}

2251. Aniline. Gas phase : 190° : nickel catalyst. Ammonia is evolved. Liquid on fractionation yields:

1. A fraction boiling about 80° (a little benzene and cyclohexane).
2. Cyclohexyl-amine, $C_6H_{11} \cdot NH_2$, b.p. 134° : 30 per cent.
3. Aniline (182°).
4. Thirty per cent dicyclohexyl-amine (252°) : 30 per cent cyclohexyl-aniline (279°) and some diphenylamine (311°).

⁹ I. G., Brit. Pat. application 295,033, convention date Aug. 6, 1927.

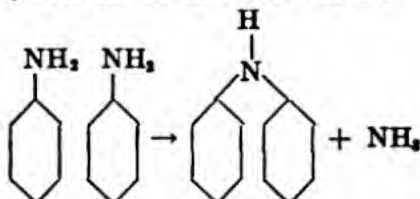
¹⁰ French Pat. 634,031, May 7, 1927, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1928, **23**, 3668; Brit. Pat. 300,285, May 4, 1927; *Chem. Age* (London), 1928, **19**, 564. Very close to this is Brit. Pat. 290,175, May 7, 1927, also to I. G.

¹¹ Can. Pat. 283,752, Oct. 2, 1928, to Lommel and Goost (to I. G. Farbenind. A.-G.) *Chem. Abst.*, 1928, **23**, 4540; Brit. Pat. 305,507, Nov. 11, 1927, to the I. G.

^{11a} U. S. Pat. 1,712,709, May 14, 1929.

^{11b} Can. Pat. 286,301, Jan. 8, 1929 (assigned to I. G.); *Chem. Abst.*, 1929, **23**, 1420.

The dicyclohexyl-amine is derived from the condensation of 2 molecules of cyclohexyl-amine by the nickel, with elimination of ammonia.



The cyclohexanyl-aniline and the diphenyl-aniline may be regarded as produced by the partial dehydrogenation of the dicyclohexyl-amine. [Sabatier: *Catalysis*, 466. Sabatier and Senderens, *Compt. rend.*, 1906, 138, 457.]

2252. With Willstätter's method (platinum-black catalyst and hydrogenation in acetic acid solution), aniline gives dicyclohexyl-amine, with only 10 per cent of cyclohexyl-amine. [Willstätter and Hatt, *Ber.*, 1912, 45, 1471.]

2253. Aniline: Hydrogenation under Pressure with Osmium.¹² *Preparation of catalyst.* Asbestos, ignited and washed with hydrochloric acid and water, was soaked in water solution of osmium tetroxide, treated with hydrazine hydrochloride, made alkaline with sodium hydroxide, heated thirty minutes on water-bath, washed with water, then with acetic acid and again with water, dried twenty-four hours at 50° C. and the drying finished by standing in a vacuum over sulphuric acid. After use the catalyst which is now in the metallic form can be regenerated with hydrogen peroxide.

Aniline. This must be purified with great care.

Procedure. Ipatiev's method was used, at 260° C., under an initial hydrogen pressure of 100 atmospheres. After eleven hours the yield was: 4 per cent benzene; 25 per cent cyclohexyl-amine; 20 per cent dicyclohexyl-amine; 5 per cent *N*-cyclohexyl-aniline and 29 per cent unchanged aniline. The evolved gases contained ammonia.

2254. Aniline: Hydrogenation under Pressure with Iridium.¹³ *Preparation of catalyst.* Asbestos, soaked in boiling water solution of ammonium chloroiridate (partly reduced to chloroiridite by alcohol), was treated slowly with formic acid and sodium or ammonium acetate, drained, washed with boiling water, dried at 110° C. and activated by heating in oxygen for some hours at 350°–400° C.

Procedure. Ipatiev's apparatus with a side-tube for collection and protection of the low-boiling products, this side-tube was water-cooled. The results are tabulated :

Catalyst	Original Aniline	Products				
		Benzene + Cyclohexane	Cyclohexylamine	<i>N</i> -cyclohexylaniline	Dicyclohexylamine	Unchanged Aniline
Iridium 2.5 g. not activated with oxygen	100	25	25	0	15	35
Iridium 2.5 g. regenerated with H ₂ O ₂ ..	100	9	40	0	15	30
Osmium 1.1 g.	50	0	45	0	33	21
Osmium 0.15 g.	50	0	14	0	6	78
Osmium 0.6 g.	50	4	35	5	20	29

¹² Sadikov and Klebanski, *Ber.*, 1928, 61B, 131; *Chem. Abst.*, 1928, 22, 1336.

¹³ *Ibid.*

2255. Toluidines are not so easily hydrogenated in the gas phase over nickel as aniline. At 200° meta-toluidine gives a complicated mixture of products. In addition to unchanged toluidine there is a little methyl-cyclohexane, b.p. 101°, a large amount of methocyclohexyl-amine $\text{CH}_3 \cdot \text{C}_6\text{H}_{10} \cdot \text{NH}_2$, b.p. 150°, having an intensely alkaline reaction and higher products (bp. 145° ^{20 mm.} and 175° ^{20 mm.}), also alkaline, which seem to be dimethocyclohexyl-amine and methocyclohexyl-aniline respectively. The catalyst is rapidly poisoned. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), 4, 387.]

2256. Methyl aniline, hydrogenated in the gas phase over nickel, at 160°–180°, gives a relatively poor yield of cyclohexyl-methyl-amine. A secondary reaction produces methylamine, with benzene or cyclohexanol. This secondary reaction increases with rise of temperature. [Sabatier and Senderens, *Compt. rend.*, 1904, 138, 1257.]

2257. Benzylamine to hexahydrobenzyl-amine and dihexahydrobenzyl-amine. Gas phase: 160°–180° nickel catalyst. Amine is prepared by passing ammonia and benzyl alcohol vapors over thoria at 330°. [Sabatier and Mailhe, *Compt. rend.*, 1911, 153, 160.] Benzylamine prepared by other methods breaks up into ammonia and toluene, when hydrogenation is attempted, even below 100°. Sabatier attributes this to a poisonous impurity (*loc. cit.*). Benzylamine over nickel at 300°–350° forms ammonia and toluene. [Sabatier, 496.]

2258. Ethylaniline to cyclohexyl-ethyl-amine (b.p. 164°). Gas phase: 160°–180°: nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1904, 138, 1257.]

2259. Dimethylaniline to cyclohexyldimethyl-amine. [*Idem, Ibid.*]

2260. Diethylaniline to cyclohexyldiethyl-amine. Gas phase: 160°–180°: nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1904, 138, 1257.]

2261. Benzylamine (technical), which cannot be hydrogenated by nickel at 170°–180°, is transformed by hydrogen at 3 atmospheres pressure and 50°–60° in the presence of colloidal platinum rapidly and quantitatively into cyclohexylmethylamine; under closely similar conditions, β -phenylethylamine gives β -cyclohexylethylamine. [Skita with Reitmayer, *Ber.*, 1924, 57B, 1977; *J. Chem. Soc. Abst.*, 1925, i, 140.]

2262. Benzyl-aniline to hexahydrobenzyl-aniline (with cyclohexyl-amine and methyl-cyclohexane). Liquid phase: 3 atmospheres: colloidal platinum: substrate dissolved in acetic acid. [Skita, *Ber.*, 1915, 48, 1685.]

2263. Aminophenols to cyclic amino-alcohols, with the Adams' platinum oxide catalyst. The hydro-chlorides of the aminophenols in aqueous solution were reduced at room temperature under 2 to 3 atmospheres pressure. The corresponding cyclohexyl-amine was also formed. In the case of *p*-dimethylaminophenol a mixture of the *cis* and *trans* isomers was obtained. The *meta* compounds yielded only a single isomer. Of the unsubstituted aminophenols only *m*-aminophenol was easily reduced: this yielded cyclohexyl-amine, dicyclohexyl-amine and *m*-cyclohexylamino-cyclohexanol and no *m*-aminocyclohexanol. [Heckel with Adams, *J. Am. Chem. Soc.*, 1925, 47, 1712.]

2264. A phenol or hydrogenated phenol is treated with ammonia or an amine in the presence of hydrogen and a hydrogenation catalyst in gaseous or liquid phase at a raised temperature, and with or without pressure. Hydroaromatic amines are obtained.¹⁴

2265. Diphenylamine gives dicyclohexyl-amine when hydrogenated by Ipatiev's method with his nickel catalyst. [*J. Russ. Phys. Chem. Soc.*, 1908, 40, 491; *Chem. Centr.*, 1908 (2), 1098.]

2265A. When diphenylamine is hydrogenated over nickel at 190°–210° with a rapid current of hydrogen in excess, cyclohexyl-aniline and dicyclohexyl-aniline are very slowly (several days) produced. Even in these conditions the molecule tends to break up, as is shown by the presence in the product of varying small amounts of ammonia, cyclohexane, cyclohexyl-amine, aniline, etc. At 250° the splitting is almost complete, ammonia and cyclohexane being the chief products. [Sabatier and Senderens, *Ann. Phys. Chim.*, 1905 (8), 4, 382.]

2266. 1-Benzyl-2-[methylamino]-6-cyclohexene-hydrobromide undergoes catalytic

¹⁴ Brit. Pat. 306,414 (convention date, Feb. 18, 1928) to I. G. Farbenind. A.-G.; *Chem. Age* (London), 1929, 412.

hydrogenation yielding 1⁴-benzyl-2⁴-[methylamino]cyclohexane. [Schöpf and Boettcher, *Ann.*, 1926, **448**, 1.]

2267. Diphenylamine (hydrochloride) to dicyclohexylamine.

2268. Triphenylamine to tricyclohexylamine and by-products of cyclohexane and dicyclohexylamine. Ethanol solutions: Adams' platinum-black catalyst. [Hiers and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 1909.]

2269. Alpha-cyclohexylamino-gamma-phenylbutyric acid to alpha-cyclohexylamino-gamma-cyclo-hexylbutyric acid. Acetic acid suspension: colloidal platinum catalyst: 45° C.: 3 atmospheres. [Skita and Wolff, *Annalen*, 1927, **455**, 17.]

2270. Cinnamylidenecyclohexylamine to cyclohexyl-gamma-phenylpropylamine. Acetic acid solution: colloidal platinum catalyst. [*Ibid.*]

2271. β -Naphthylamine hydrogenated over nickel in the gas phase (200 hours) gave a mixture of ammonia, tetrahydronaphthalene, dihydronaphthalene (traces), naphthalene (traces), β -aryl-tetrahydro-naphthylamine and β,β -di-aryl-tetrahydronaphthylamine. [Tohoru Hara, *Mem. Coll. Sci. Kyoto, Imp. Univ.*, 1923, Series 7A, No. 6, 403, *Chem. Abst.*, 1923, **17**, 2577.]

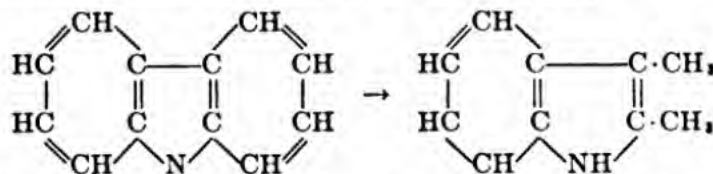
2272. Hydrogenation of Naphthylamines. *ar*-tetrahydronaphthylamine derivatives are made by subjecting *N*-substituted naphthylamines to catalytic hydrogenation. The hydrogenated naphthylamines themselves may be made by starting with an acetyl derivative and subsequently saponifying.¹⁸

2273. Phenylhydrazine, hydrogenated over nickel above 210°, yields chiefly ammonia and aniline (80 per cent), with cyclohexyl-amine, dicyclohexyl-amine, benzene and cyclohexane. [Sabatier and Senderens, *Bull. Soc. Chim.*, 1906 (3), **35**, 259.]

2274. Cyclohexylidene azine to hydrazocyclohexane. Colloidal platinum catalyst: hydrogen pressure, 2 atmospheres. [Harkins and Lochte, *J. Am. Chem. Soc.*, 1924, **46**, 450.]

2275. Phthalimide to hexahydrophthalimide. Liquid phase: platinum-black catalyst. [Willstätter and Jacquet, *Ber.*, 1918, **51**, 767.]

2276. Carbazole (diphenylene imide) to $\alpha\beta$ -dimethyl-indol.



Gas phase: 8-10 atmospheres: 200°: twelve to eighteen hours: nickel catalyst. [Padoa and Chiaves, *Lincei*, 1907, **16** (2), 762; *Chem. Centr.*, 1908 (1), 649.]

2277. Carbazoles. 6:9-Dimethyl-1:2:3:4-tetra-hydrocarbazole hydrogenated in decalin with a nickel catalyst at 240° yields a mixture of 6:9-dimethyl-1:2:3:4:5:6:7:8-octahydrocarbazole, and dimethyldodecahydrocarbazole.

3:9-Dimethyl-1:1:3:4-tetrahydrocarbazole gives the same octa- and dodeca-compounds.

9-Methyl-1:2:3:4-tetrahydrocarbazole energetically hydrogenated gives a mixture of unchanged substrate, with 9-methyloctahydrocarbazole and 9-methyldodecahydrocarbazole.

Hydrogenation of tetrahydrocarbazoles occurs at the benzenoid nucleus. [von Braun and Schörnig, 1925, *Ber.*, **58B**, 2156.]

2278. 2-Acylamino-9,10-anthrahydro-quinone ethers and esters in which the acyl group is the residue of an aliphatic carboxylic acid, such as acetic or formic acid, are formed by the catalytic hydrogenation of a 2-acylaminoanthraquinone and etherifying or esterifying the resulting leuco compound. [Brit. pat. 297,042, Apr. 13, 1927, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1929, **23**, 2447.]

¹⁸ Brit. Pat. 276,571, Feb. 24, 1927, to Soc. Anon. pour l'Ind. Chim. à Bâle; *Chem. Abst.*, 1928, **22**, 2379.

CHAPTER XXIII

HYDROGENATION OF TERPENES

AND OF COMPOUNDS CONVENIENTLY CLASSED WITH TERPENES

I

2300. Aromandrene. This sesquiterpene from eucalyptus oil is reduced to dihydroaromandrene under the following conditions: Six per cent solution in methanol; colloidal palladium catalyst (Paal); Skita's apparatus; hydrogen pressure slightly above atmospheric. [Briggs and Short, *J. Chem. Soc.*, 1928, 2527.]

2301. Azulene ($C_{15}H_{10}$) from coal-tar or from chamomile oil, to $C_{15}H_{14}$. Alcohol solution: colloidal palladium catalyst: room temperature: atmospheric pressure: fifteen hours with shaking. [Ruhemann, Levy, *et al.*, *Ber.*, 1927, 60, 2467.] Azulene is a blue hydrocarbon which is obtained by steam distillation of powdered yellow chamomile flowers. It does not exist preformed in the flowers.

2301A. Sesqui-terpene B. (from lignite tar), $C_{15}H_{14}$, apparently monocyclic, to $C_{15}H_{16}$. Vapor phase at 180° over nickel alumina catalyst. [*Ibid.*]

2302. Chamazulene to octahydrochamazulene. Acetic acid solution: colloidal platinum catalyst.

2303. Guaiazulene yields octahydroguaiazulene.

2304. Guaiene, on mild hydrogenation, yields dihydroguaiene: on energetic reduction tetrahydroguaiene results. [Ruzicka and Rudolph, *Helv. Chim. Acta*, 1926, 9, 118.]

2305. Camphenes to Camphanes. The camphanes produced by the hydrogenation of camphenes seem to differ according to the origin of the latter. From pinene hydrochloride Lipp prepared a camphene which, on hydrogenation at 170° – 190° C., in presence of nickel gave a mixture of a solid isocamphane melting at 65° – 67° C. and a liquid isocamphane boiling at 150° C.

2306. Vavon, with platinum-black catalyst, working in ether solution, obtained a dihydrocamphene melting at 87° . [*Compt. rend.*, 1909, 149, 997.]

2307. Using colloidal palladium Skita and Meyer prepared a camphane with a melting-point of 53° . [*Ber.*, 1912, 45, 3579.]

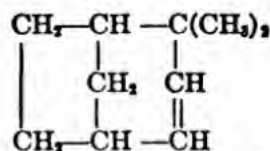
2308. With a nickel catalyst, Sabatier and Senderens, hydrogenated (with difficulty) a camphene, of unknown origin, at 165° – 175° , to a camphane, b.p. 164° . [Sabatier and Senderens, *Compt. rend.*, 1901, 132, 1256.]

2308A. An inactive camphene (m.p. 47° – 49°) yielded a camphane melting at 60° , by hydrogenation over nickel. [Nametkin and Abaumovskaya, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 414; *Chem. Abst.*, 1916, 10, 45.]

2308B. Ipatiev's method with the copper catalyst seems to give the same results as those reported by Lipp. Camphene gives two hydrides, a solid melting at 66° and a liquid boiling at 162° . [Ipatiev and Drachusoff, *J. Russ. Phys. Chem. Soc.*, 1911, 42, 1563; *Chem. Centr.*, 1911 (1), 1292.]

2308C. With the "nickel oxide" catalyst at 240° , in ten to fifteen hours camphene gives an iso-camphane melting at 57° and boiling at 162.5° . [Ipatiev, *Ber.*, 1912, 45, 3210.]

2309. Endocamphene



to dihydroendocamphene. [Götzen and Reinartz, *Ann.*, 1927, **453**, 1; *Chem. Abst.*, 1927, **21**, 2891.]

2310. *d*-Cadinene (sesquiterpene from West Indian sandalwood oil) to tetrahydrocadinene. Solution in 96 per cent alcohol : platinum-black catalyst. [Deussen and Avramoff, *J. prakt. Chem.*, 1928, **120**, (ii), 119.]

2311. Carvomenthene to menthane, see under Limonene.

2312. Caryophyllene to dihydrocaryophyllene. Palladium or nickel catalyst. [Deussen, *J. prakt. Chem.*, 1926, **114**, ii, 63]. Cf. *Idem*, *Ann.*, 1912, **388**, 136 : colloidal palladium : methyl alcohol solution.

2312A. γ -Caryophyllene to γ -dihydrocaryophyllene. [*Ibid.*, 1927, **117**, (ii), 273.]

2312B. Ethyl- γ -caryophyllenecyclopropane-carboxylate gives a dihydro-derivative. [*Ibid.*]

2313. *l*- α -Curcumene to hexahydro- α -curcumene.

2313A. *l*- β -Curcumene to *l*-hexahydro- β -curcumene. [Rao and Simonsen, *J. Chem. Soc.*, 1928, 2496.]

2314. Eudesmene to tetrahydrocompound $\text{C}_{15}\text{H}_{28}$, platinum-black catalyst : glacial acetic acid solution. [Semmler and Risse, *Ber.*, 1913, **46**, 2303.]

2315. Ferulene, $\text{C}_{15}\text{H}_{26}$, from gum ammoniac oil in liquid phase, platinum-black catalyst, takes up 2H_2 . [Semmler, Jonas and Roenisch, *Ber.*, 1917, **50**, 1823.]

2316. A sesquiterpene (?) derived from *geraniol* by treatment with sulphuric acid yields, on hydrogenation in presence of palladium catalyst, a hydrocarbon $\text{C}_{15}\text{H}_{28}$. [Thoms, *Oesterr. Chem. Ztg.*, 1926, **29**, 228.]

2317. Limonene to dihydrolimonene. Ipatiev's method : "copper or copper oxide" catalyst : 300° : 120 atmospheres. The hydrogenation continues with the formation of menthane. [Ipatiev, *Ber.*, 1910, **43**, 3546.]

2318. In the gas phase, at ordinary pressures, at 169° – 170° C., with a nickel catalyst, limonene hydrogenates to menthane. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1256. Cf. Vavon, *Compt. rend.*, 1911, **152**, 1675, and 1909, **149**, 999. With a copper catalyst dihydrolimonene is formed, exclusively. *Ibid.*, 1255.]

In ether solution, in the cold, with 25 per cent of its weight of platinum-black, limonene readily adds H_2 , forming carvomenthene, b.p. 175° , and then another H_2 with formation of menthane. [Vavon, *Bull. Soc. Chim.*, 1914, (4), **15**, 282.]

2319. Escourrou. Selective reduction under reduced pressure [in vapor phase over nickel and platinum oxide catalysts] of citral, geraniol and limonene. [*Bull. Soc. Chim.*, 1928 (iv), **43**, 1204. See abstract in para. 2404 under citral.]

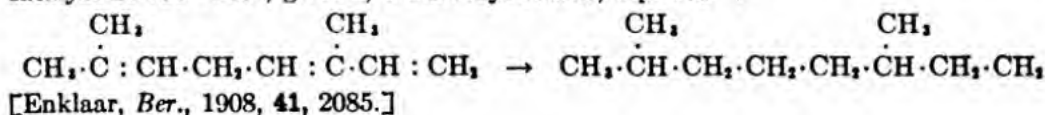
2320. Menthene to menthane.¹ Gas phase : 175° : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1256.]

2320A. Menthene to menthane and *p*-cymene. Vapor phase over copper at 290° – 300° C. [Komatsu and Kurata, *Mem. Coll. Sci. Kyoto*, 1928, **11A**, 164.]

d-Limonene to cymene. Vapor phase over copper at 280° – 300° . But at 200° menthane, dipentene and carvomenthene are also formed. [*Ibid.*]

d- β -Phellandrene to cymene (85 per cent) and some menthane. Vapor phase over copper at 300° C. [*Ibid.*, cf. Rupe and Schäfer, *Helv. Chim. Acta*, 1928, **11**, 463; Sabetay and Bléger, *Bull. Soc. Chim.*, 1928 (iv), **43**, 839.]

2321. 2, 6-Dimethyl-octatriene (2, 5, 7) (ocimene from oil of basil), over a nickel catalyst at 130° – 140° , gives 2, 6-dimethyl-octane, b.p. 158° :



¹ See under Limonene.

2322. Pinene to dihydropinene. Gas phase : 170°–180° : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1256.]

2323. By Ipatiev's method, using "nickel oxide" catalyst, pinene is hydrogenated at 265° to pinane and at 300° to menthane. [Sabatier: *Catalysis*, **591**.] With a copper catalyst at 300°–350° and at 100 + atmospheres, pinene yields pinane on hydrogenation.

2324. With colloidal palladium catalyst under 2 atmospheres pressure, pinene hydrogenates to pinane. [Sabatier: *Catalysis*, **552**.]

2324A. With 15 g. platinum-black catalyst 500 g. pinene is hydrogenated in twenty-four hours to dihydropinene, b.p. 166°. [Vavon, *Compt. rend.*, 1909, **149**, 997.]

2325. A diterpene $C_{20}H_{32}$ (from German turpentine oil) hydrogenated in presence of platinum gave octahydroditerpene $C_{20}H_{40}$ (monocyclic?).

2325A. From the same source a sesquiterpene alcohol $C_{15}H_{26}O$ was obtained which on hydrogenation gave a saturated dihydro compound. (Wienhaus, *Förh. III nord. Kemistmötel*, 1928, 211; *Brit. Chem. Abst.*, 1929, 191A.)

2326. Contact Transformation of α -Pinene.² Passage of *l* or *d*- α -pinene over palladized asbestos at 190°–200° in an atmosphere of carbon dioxide causes the production of cymene and a dihydropinene, b.p. 166.5°–167.5°, d_4^{18} 0.8467, n_D^{18} 1.4589, identical with the product obtained by catalytic hydrogenation of pinene in the presence of nickel. The mixture of cymene and dihydropinene is transformed by hydrogen in the presence of palladium at 200° into menthane and dihydropinene. Hydrogenation of pinene at 200° in the presence of palladized asbestos gives a dihydropinene identical with that described above, whereas at 157°–158° a different dihydropinene, b.p. 169°–169.5° (corr.), is produced. The mechanism of the catalytic reduction of pinene depends, therefore, on the temperature and nature of the catalyst.³

2327. According to Richter and Wolff (*Ber.*, 1926, **59** (B), 1733], treatment of α -pinene with hydrogen in the presence of palladium-black from palladium chloride affords mainly a mixture of α -pinene and pinane instead of isopinene recorded by Zelinski. On the other hand, β -pinene is quantitatively isomerized to α -pinene by palladium saturated with hydrogen and subsequently reduced to pinane. Palladium alone does not effect the transformation.⁴

2328. The statement by Zelinski to which reference is here made is that when palladium-black made from the subchloride is suspended in ether, in an atmosphere of hydrogen, and pinene is added, on passing a current of hydrogen, isopinene (b.p. 158.5°–159.5°) results, the hydropinene first formed being dehydrogenated. If, however, palladium prepared from palladium ammonium chloride is used hydropinene results.⁵ It is conceivable that the difference may be determined by the presence or the exclusion of oxygen.

2329. Sabinene to thujane. Platinum-black catalyst : 25–50 atmospheres in sealed tube : forty-eight hours : at room temperature. [Tchougaeff and Fomin, *Compt. rend.*, 1910, **151**, 1058.]⁶

2330. Santene to dihydrosantene. [*Chem. Abst.*, 1927, 237.]

2331. Sylvestrene to menthane. Gas phase : 180° C. : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, **132**, 1256.]

2332. Thujene and thujane to $C_{10}H_{20}$ (possibly 1 : 2- or 1 : 3-dimethyl-3-*iso*-propyl-cyclopentane). Vapor phase : 155° C. : palladium-charcoal.

2333. Thujene at 197°–200° C. over palladium-asbestos gives cymene, thujane and a cyclic hydrocarbon, $C_{10}H_{20}$. [Zelinski and Kasanski, *Ber.*, 1927, **60B**, 1096.]⁷

2334. α -Thujene to hexahydrocymene. Gas phase : 125° : nickel catalyst. [Zelinski, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 768.]

² Zelinski, *Ber.*, 1924, **58**, B, 864.

³ *J. Chem. Soc. Abst.*, 1925, i, 821.

⁴ *Brit. Chem. Abst.*, 1926, 1148 A.

⁵ *Ber.*, 1911, **44**, 2782.

⁶ See paras. 2332, 2333, 2334, 2335.

⁷ Cf. para. 2329.

2335. α -Thujene to thujane, b.p. 157°. In liquid phase : 25–50 atmospheres : platinum-black catalyst : two days. [Tchougaeff and Fomin, *Compt. rend.*, 1910, **151**, 1058.]

2336. Isozingiberene (bicyclic) with platinum-black catalyst, glacial acetic acid solution : takes up 2H₂, forming tetrahydroisozingiberene. [Semmler and Becker, *Ber.*, 1913, **46**, 1814.] Zingiberene, in some conditions, forms monocyclic hexahydrozingiberene. [*Ibid.*]

2337. α -Amirol (a sesquiterpene alcohol from West Indian sandalwood oil) to α -dihydroamirol. Alcohol solution : palladized calcium carbonate catalyst. [Deussen and Avramoff, *J. prakt. Chem.*, 1928, **120** (ii), 119.]

2338. Betulol, C₁₅H₂₄O, to the alcohol, C₁₅H₂₆O. Liquid phase, solution in absolute ether : platinum-black catalyst. [Semmler, Jonas and Richter, *Ber.*, 1918, **51**, 417.]

2339. Cadinol to dihydrocadinol. Ethyl acetate solution : 70° : platinum-black catalyst. [Ruzicka and Stoll, *Helv. Chim. Acta*, 1924, **7**, 84; *Chem. Abst.*, 1924, 1282.]

2340. Camphor to borneol. Ipatiev's method : "nickel oxide" catalyst : 350°. [Sabatier: *Catalysis*, 591.]

2341. Camphor to iso-camphene, m.p. 63° (dehydration plus hydrogenation.) Ipatiev's method : 110 atmospheres : 220° : forty hours. [Ipatiev and Matov, *Ber.*, 1912, **45**, 3205.]

2342. The oxidation of *d*- and *l*-borneols to camphor takes place without any side reactions when reduced copper at 200°–220° is employed as a catalyst. Copper oxide, prepared from copper nitrate and sodium hydroxide and reduced with hydrogen at 200°, furnishes the best copper catalyst. No borneol is formed when camphor vapor and hydrogen are together passed over reduced copper. [Masumoto, *Mem. Coll. Sci.*, Kyoto, 1925, **9**, 219, *Brit. Chem. Abst.*]

2342A. Camphor to isoborneol and isocamphane. Glacial acetic acid solution : platinum-black catalyst. [Vavon and Peignier, *Bull. Soc. Chim.*, 1926, **39** (iv), 924.]

2343. Camphor to isoborneol (and some borneol). Platinum-black catalyst. [Vavon and Peignier, *Compt. rend.*, 1925, **181**, 183.]

2344. Camphor enol ethyl ether to camphor bornyl ethyl ether and a small quantity of acid reaction products. [Bredt-Savelsberg and Rumschedit, *J. prakt. Chem.*, 1927, **115**, 235; *Chem. Abst.*, 1927, **21**, 1807.]

2345. Phenylacetylenylborneol $\left(\text{C}_6\text{H}_5 \cdot \begin{array}{c} \text{CH}_3 \\ | \\ \text{C}(\text{OH}) \cdot \text{C} : \text{C} \text{C}_6\text{H}_5 \end{array} \right)$ to styryl borneol $\left(\text{C}_6\text{H}_5 \cdot \begin{array}{c} \text{CH}_3 \\ | \\ \text{C}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_5 \end{array} \right)$. Solution in aqueous alcohol and ethyl acetate : nickel catalyst. [Rupe, *Ann.*, 1924, **436**, 184.]

2346. Doremol to the saturated alcohol. Liquid phase : platinum-black catalyst.

2347. Doremone to tetrahydrodoremone. Liquid phase : platinum-black catalyst. [Semmler, Jonas and Roenisch, *Ber.*, 1917, **50**, 1823.]

2348. Eugenol H₃C(HO)C₆H₃·CH₂CH : CH₂ and iso-eugenol, H₃C(HO)C₆H₃·CH : CH·CH₃, with Ipatiev's method with his "nickel oxide" catalyst, at 29°, give methoxy-propyl-phenol, CH₃O(OH)C₆H₃·CH₂·CH₂·CH₃, but at 195° the phenolic hydroxyl is eliminated and the chief product is methoxy-propyl-cyclohexane. [Ipatiev, *Ber.*, 1913, **46**, 3589.]

2349. With a nickel catalyst at 60° and 15 atmospheres eugenol gives methoxy-propyl-phenol. At 150° the aromatic nucleus is hydrogenated also. [Brochet and Bauer, *Bull. Soc. Chim.*, 1915, (4), **17**, 54.]

2350. According to Madinaveitia and Blanes [*Soc. Españ. Fís. Quím.*, 1913, **10**, 381; *Chem. Abst.*, 1913, **7**, 3500], with palladium-black catalyst eugenol adds H₂, producing "dihydroeugenol" (methoxy-propyl-phenol?). With platinum-black, methoxy-propyl-cyclohexanol results. On the other hand, Fournier, using a platinum-black catalyst derived isopropyl guaiacol from both eugenol and iso-eugenol. [*Bull. Soc. Chim.*, 1910 (4), **7**, 23.]

2351. Benzoyl derivative of 2-methoxy-4- Δ^8 -butenyl-phenol (homoeugenol) to 2-methoxy-4-*n*-butylphenyl benzoate. Palladium charcoal catalyst. [Mannich and Merz, *Arch. Pharm.*, 1927, **265**, 104.]

2352. Farnesol, $C_{15}H_{32}O$, in liquid phase, platinum-black catalyst, takes up $3H_2$ to form *dl*-hexahydrofarnesol. [Semmler, Jonas and Roenisch, *Ber.*, 1917, **50**, 1823.] In methanol with palladinized calcium carbonate hydrogenation of farnesol yields 40 per cent, with palladous chloride 80 per cent of farnesane (β γ -trimethyldodecane). [Fischer, *Ann.*, 1928, **464**, 69.] Farnesyl acetate in ethyl acetate solution with palladinized calcium carbonate gives some farnesane, but the chief product is hexahydrofarnesol ($\delta\eta$ -trimethyl dodecanol). [*Ibid.*]

2353. Geraniol on complete hydrogenation yields an alcohol that seems identical with that obtained by the interaction of $\gamma\eta$ -dimethyloctylamine. [Sabetay and Bieger, *Bull. Soc. Chim.*, 1928, (iv), **43**, 839.]

2353A. Suzuki [*Bull. Inst. Phys. Chem. Research*, 1929, **8**, 44, *Abst.* **2**, 3; *Chem. Abst.*, 1929, **23**, 186; *Brit. Chem. Abst.*, **1929**, 297A], hydrogenated geraniol and citronellal with nickel catalyst and compared the rates of hydrogen addition. The first molecule of hydrogen was taken up by citronellal more rapidly than by geraniol, the second molecule was added very slowly. A trace of ferrous sulphate slowed the hydrogenation of geraniol but had little effect with citronellal. The products in each case seem to have been impure citronellol with some dehydrocitronellol. Experimental conditions were: 5 g. substance in 25–100 cc. of 70–80 per cent alcohol; 2–6 g. catalyst; temperature 25°–28°C.; hydrogen pressure 1.1 atmosphere.

2354. Geraniol gives racemic "citronellol (Ni)" when shaken at 80°–95° with hydrogen in presence of a nickel catalyst. This product differs from the product of platinum catalysis ("citronellol (Pt)") in its higher content of the α form. [Grignard and Escourrou, *Bull. Soc. Chim.*, 1925, **37**, 546.]

2355. β -Geraniol is hydrogenated by shaking its solution in anhydrous ether with platinum-black and hydrogen, until 1 mol. of hydrogen is absorbed for each mol. of geraniol. The product is racemic rhodinol: it is the beta-form. [*Ibid.*, 542. See also: Longuinod and Margollis, *Bull. Soc. Chim.*, 1925, iv, **45**, 156; *Brit. Chem. Abst.*, **1929**, 538A.]

2355A. Geraniol [as well as other perfumes, such as ionones and methylionones] is said to have its color and odor improved by partial hydrogenation with hydrogen and nickel catalyst [or with sodium ethylate, or with aluminum amalgam, or with zinc dust.]^a

2356. Geraniol, 2, 6-dimethyl-octadiene (2, 6) ol (8) to 2, 6-dimethyloctanol (with some 2, 6-dimethyl octane). Gas phase: 130°–140°: nickel catalyst. [See also under citral, para. 2404.]

2357. In liquid phase, with nickel catalyst at 15 atmospheres and 70°, geraniol gives 2, 6-dimethyl-octanol. [Brochet and Bauer, *Bull. Soc. Chim.*, 1915, (4), **17**, 50.]

2358. By Ipatiev's method, with palladium reduced from the chloride by formate as catalyst (about 3 per cent by weight of substrate), at 110° and 100 \pm atmospheres, geraniol gives the dimethyl-octanol and some dimethyl-octane. [Sabatier, **595**.]

2359. Platinum-black catalyzes this reaction very slightly, the formation of the alcohol taking several days. [Willstätter and Meyer, *Ber.*, 1908, **41**, 1475.]

By Paal's method in methanol solution, Ishizaka obtained tetrahydrogeraniol. [*Ber.*, 1914, **47**, 2453; *Chem. Abst.*, 1915, **9**, 76.]

2360. Isosmyl-carvol, with platinum-black catalyst, takes up $2H_2$ and yields the saturated alcohol. [Semmler, Jonas and Oelsner, *Ber.*, 1917, **50**, 1838.]

2361. Limonene-1:2-diol to menthane-1:2-diol (1:2-dihydroxymenthane). Platinum-black catalyst. [Meerwein, *J. prakt. Chem.*, 1926, **113**, ii, 9.]

2362. Linalool, 2, 6-dimethyl-octadiene (2, 7)-ol (6) to 2, 6-dimethyloctanol (and a little 2, 6-dimethyloctane). Gas phase: 130°–140°: nickel catalyst. [Enklaar, *Rec. Trav. Chim. Pays Bas*, 1908, **27**, 411; *Ber.*, 1908, **41**, 2085.]

^a French Pat. 643,352, Nov. 4, 1927, to I. G. Farbenind. A.-G.

2363. With platinum-black catalyst in liquid phase, at room temperature, the same product is obtained. [Barvier and Locquin, *Compt. rend.*, 1914, **158**, 1555.]

2364. With a nickel catalyst, in liquid phase, under 15 atmospheres at 70°, the same hydrogenation occurs. [Brochet and Bauer, *Bull. Soc. Chim.*, 1915, (4), 17.]

2365. Diisopulegyl ether, $C_{20}H_{34}O$, is reducible catalytically to the saturated ether.

2366. Isopulegol to *l*-menthol. Glacial acetic acid solution: platinum-black catalyst.

2367. An ether, $C_{20}H_{34}O_2$, obtained in small yield by treatment of citronellal with dilute sulphuric acid, is hydrogenated catalytically to a compound $C_{20}H_{38}O_2$. [Horiuchi, *Mem. Coll. Sci.*, Kyoto, 1928; **11**, A, 171.]

2368. Rhodinol to dihydrorhodinol (γ -dimethyloctanol). Fokin-Willstätter method. [Sabetay and Bléger, *Bull. Soc. Chim.*, 1928, (iv), **43**, 839.]

2369. Safrol to hydrosafrol, by hydrogenation in presence of platinum-black or nickel. [Kafuku, *J. Pharm. Soc.*, Japan, 1925, **521**, 609; *Chem. Abst.*, 1926, 400.] Safro-eugenol to hydrosafro-eugenol. [*Idem*, *Ibid.*]

2370. Isosafrol and safrol to dihydrosafrol. Gas phase: 200° C.: nickel catalyst. [Henrard, *Chem. Weekblad.*, **4**, 630-632; *Chem. Centr.*, 1907 (2), 1512.]

2371. The same hydrogenation can be effected in the liquid phase, with a platinum-black catalyst. [Fournier, *Bull. Soc. Chim.*, 1910 (4), **7**, 23.]

2372. Also, by Ipatiev's method, using a "nickel oxide" catalyst, under 50 atmospheres at 93°, the dihydrosafrol (b.p. 228°) is obtained. By longer treatment at 180° a product is obtained which appears to be methoxy-propyl-cyclohexane, b.p. 207°. [Ipatiev, *Ber.*, 1913, **46**, 3589.]

2373. Isosafrol, 33 per cent solution in alcohol, with 19 per cent nickel catalyst, at 65°, also hydrogenates to dihydrosafrol, at atmospheric pressure. [Brochet and Bauer, *Bull. Soc. Chim.*, 1915 (4), **17**, 50. Cf. Brochet, *Compt. rend.*, 1914, **159**, 326.]

2374. Terpineol to hexahydrocymene. Gas phase: 150°: nickel catalyst. [Haller and Martine, *Compt. rend.*, 1905, **140**, 1303.]

2375. α - and β -terpineols, in the liquid phase, under 2 atmospheres pressure, with a colloidal palladium catalyst, are hydrogenated to dihydroterpineols. [Wallach, *Annalen*, 1904, **336**, 37.]

2375A. Alphaterpineol on hydrogenation yields, on fractional distillation, a solid identical with di-hydro alphaterpineol, a tertiary saturated alcohol from American pine oil. [Zeitschol and Schmidt, *Ber.*, 1927, **60B**, 1372.]

2376. Thymoquinol [$C_{15}H_{17}(CH_3)C_6H_4(OH)_2$] to menthane-diol (2, 5), m.p. 112°. Gas phase: 190°-200°: nickel catalyst. [Henderson and Sutherland, *J. Chem. Soc.*, 1910, **97**, 1616.]

2377. The condensation products of alkylated phenols with ketones are hydrogenated to obtain thymols, its isomers and homologs. A metal phenolate may be present in addition to the hydrogenation catalyst, to reduce the decomposition temperature. E.g., the condensation product of acetone and meta-cresol is hydrogenated in presence of a nickel catalyst and of aluminum-3-methyl-6-isopropylene-phenolate to obtain thymol and then stereoisomeric menthols.⁹

2377A. By acting on these same condensation products with hydrogen under pressure, in presence of a catalyst and a diluent (menthane) at 280° C., thymol or its isomers and homologs are produced.¹⁰

⁹ Brit. Pat. application 276,010, convention date Aug. 16, 1926, by Chem. Fab. auf Aktien, vorm. E. Schering; *Chem. Age* (London), 1927, **17**, 373. Can. Pat. 281,117, June 19, 1928, to Jordan and same assignees.

¹⁰ Can. Pat. 281,115, June 19, 1928, to Jordan, Schöellerr and Clerc, assigned to Chem. Fab. auf Aktien, vorm. E. Schering. Cf. U. S. Pat. 1,706,784, Mar. 26, 1929; *Chem. Abst.*, 1929, **23**, 2191; Brit. Pat. 279,857, Oct. 26, 1926, to Chem. Fab. auf Aktien, vorm. E. Schering; Brit. Pat. 279,855 of same date, to same patentee; Can. Pat. 281,120, June 19, 1928, and 281,119 of the same date, to same patentees and assignees. For variations see: Brit. Pat. 276,010, Aug. 11, 1927, to Chem. Fab. auf Aktien, vorm. E. Schering, 280,956, Nov. 21,

2378. Thymol synthesis. 3-Methyl-6-isopropylphenol hydrogenated at a high temperature with a catalyst gives 3-methyl-6-isopropyl phenol (thymol).¹¹

2379. Oxythymol is heated with hydrogen in presence of a hydrogenating catalyst and a porous support such as fuller's earth. Two or eight atomic proportions of hydrogen are absorbed with formation of thymol and menthol.¹²

2380. Thymol to menthol. Fifteen atmospheres pressure: 160°–170°: nickel-kieselguhr catalyst. Product washed with caustic soda to remove unchanged thymol. The crude menthol is either oxidized in acetic acid solution with chromic acid to menthone, and the menthone reduced in alcoholic solution with sodium, or it is converted into phthalate and the menthol recovered by saponification.¹³

2380A. Thymol to menthol. Liquid phase: 5 to 30 atmospheres: 200° C.: Nickel, platinum, palladium, or cobalt catalyst.¹⁴

2380B. Thymol, menthone and iso-menthone to a mixture of inactive neomenthol, neoisomenthol, and inactive menthol.¹⁵

2380C. Inactive neomenthol and inactive neoisomenthol to inactive menthol by catalytic hydrogenation either directly or after dehydrogenation. The catalysts used were nickel cobalt, copper, platinum and palladium.¹⁶

2380D. Thymol is heated with hydrogen and hydrogenation catalysts under pressure: inactive menthol is separated from the mixture of liquid menthols and the latter is converted by dehydrogenation into a mixture containing menthones: this mixture is then hydrogenated under pressure.¹⁷

2381. When piperitone or menthone is catalytically hydrogenated, the product is composed of a mixture of a crystalline solid (*i*-menthol) and a residual oil, which apparently consists of an isomeride of menthol. If this liquid is heated in presence of hydrogen and the catalyst for several hours at 110°–120° C., it is partially converted into the crystallizable substance. The yield of the latter can therefore be increased by dissolving fresh piperitone or menthone in the oily filtrate of a previous batch. Thus, when piperitone (150 lb.) is treated with hydrogen at 30–70 lb.-sq. in. pressure and at 130°–160° C. in presence of nickel catalyst (2 lb.) until no more absorption takes place, the mixture obtained, on cooling to 10°, deposits crystals equivalent to about 30 per cent of the piperitone, but when the mixture, after hydrogenation, is stirred for several hours at 120° C. in an atmosphere of hydrogen and in presence of the catalyst, the yield of crys-

1927, and 280,924, Nov. 16, 1927, to Schering-Kahlbaum A.-G. (*Brit. Chem. Abst.*, 1929, B. 237), 293,001, June 29, 1927, to Schering-Kahlbaum A.-G. (*Chem. Abst.*, 1929, 23, 1142), French Pat. 641,437, Aug. 9, 1927, to Chem. Fab. auf Aktien, vorm. E. Schering (*Chem. Abst.*, 1929, 23, 1142). For separation of the products see: Brit. Pat. 285,833, Feb. 22, 1927, to Schering-Kahlbaum A.-G. For conversion and purification see: Brit. Pats. 289,125, 289,126, Jan. 17, 1927, to Rhein. Kampfer Fab. Ges., *Chem. Abst.*, 1929, 23, 611; Swiss Pat. 126,585, Jan. 7, 1927, to the same patentees, *Ibid.*; U. S. Pat. 1,672,346, June 5, 1928, to Schöllkopf (assigned to Rhein. Kampfer Fab. Ges.), *Chem. Abst.*, 1928, 22, 2573.

¹¹ Can. Pat. 278,728, Mar. 30, 1928, to Schöellerr and Jordan; *Chem. Abst.*, 1928, 22, 2756. Cf. French Pat. 636,267, June 20, 1927, to Chem. Fab. auf Aktien, vorm. E. Schering, *Chem. Abst.*, 1929, 23, 156.

¹² Brit. Pat. application 301,087 (convention date, Nov. 24, 1927), by Schering-Kahlbaum A.-G.

¹³ Austerwehl, Brit. Pat. 239,527, Aug. 21, 1923.

¹⁴ U. S. Pat. 1,629,002, May 17, 1927, to Schöllkopf.

¹⁵ Brit. Pat. application 285,394 (convention date, Feb. 15, 1927), by Rhein. Kampfer Fab. Ges.

¹⁶ Brit. Pat. application 285,403, by same; *Ibid.* Cf. U. S. Pat. 1,629,002, May 17, 1927, to Schöllkopf; *Chem. Abst.*, 1927, 21, 2136, and U. S. Pat. 1,625,771, Apr. 19, 1927, to Schöllkopf. An earlier patent (Brit. Pat. 231,827, Apr. 4, 1924, to the Rhein. Kampfer Fab. A.-G.) provides for the separation of the isomenthol by distillation. It is then either: (1) subjected to further hydrogenation; or (2) first dehydrogenated to isomethone and the latter hydrogenated.

¹⁷ U. S. Pat. 1,704,630, Mar. 5, 1929, to Schöllkopf (assigned to Rhein. Kampfer Fab. G. m. b. H.; *Chem. Abst.*, 1929, 23, 1920).

talline product is much greater. When the separated oil is similarly treated, up to 50 per cent is converted into the crystalline substance.¹⁸

2382. Tolyl-dimethyl carbinol hydrogenated over nickel of slight activity, at 400° C., gives cymene (methyl-isopropyl-benzene, b.p. 175°). This cymene, over an active nickel below 180°, may be regularly hydrogenated to menthane (hexahydrocymene). [Smirnov, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1374.]

2383. Methysticin to dihydromethysticin : alcohol solution : colloidal palladium : room temperature : atmospheric pressure. Methysticin is a product from Kawa root (*Piper methysticum*). Methysticol to tetrahydromethysticol. [Borsche, 1927, *Ber.*, **60**, 982.]

2384. *p*-Menthene oxide to *p*-menthane. Willstätter's method (platinum- or palladium-black activated by oxygen.) [Kötz and Busch, *J. pr. Chem.*, 1928, **119** (ii), 1.]

¹⁸ *J.S.C.I.*, **1925**, 900B; Brit. Pat. 238,314, May 21, 1924 (addition to 213,991), to Howards and Sons, Ltd., and Blagden.

CHAPTER XXIV

HYDROGENATION OF TERPENES

AND OF

COMPOUNDS CONVENIENTLY CLASSED WITH TERPENES

II

2400. Citral. Citral, in ether solution, with platinum-black catalyst, gives a mixture of 2,6-dimethyl-octane and 2, 6-dimethyloctanol .8 [Vavon, *Ann. chim.*, 1914 (9), 1, 144.] The use of aqueous alcohol solution gives much higher proportion of the alcohol.

2401. By Ipatiev's method, using palladium catalyst, at 110°, with continuous shaking, citral yields decanol with some decane.

2402. Skita, with colloidal platinum obtained citronellal, citronellol and a condensation product $C_{10}H_{20}O$. [*Ber.*, 1909, 42, 1634.]

2403. Selective Reduction of Citral by Means of Platinum-Oxide-Platinum-Black and a Promoter.¹ When treated with hydrogen in presence of platinum oxide-platinum-black, citral is partly reduced to tetrahydrogeraniol. Reactivation of the catalyst by shaking with air causes the reaction to go further, but the reduction cannot be completed, as successive reactivations cause coagulation of the catalyst. In presence of a trace of ferrous sulphate, reduction proceeds progressively to tetrahydrogeraniol. If the reaction is interrupted when successive mols of hydrogen have been absorbed, the products are pure geraniol, citronellol, and tetrahydrogeraniol, respectively. The action of zinc acetate is similar to that in the reduction of cinnamaldehyde, and the concentration of this promoter can be adjusted to cause the reaction to cease when either 1 or 2 mols of hydrogen have been absorbed by the citral, but in such cases the rate of reduction is considerably reduced.²

2404. Citral is converted into citronellal over nickel at 190° under reduced pressure, and also under ordinary pressure at 180°. Limonene at 20 mm. undergoes 10 per cent hydrogenation, but for further catalysis to take place the pressure must be raised to 150–200 mm. Geraniol at ordinary pressure and at 160°–165° with platinum oxide as catalyst gives *p*-menthane in addition to the products obtained by Enklaar; under reduced pressure, citronellol is obtained, at which stage reduction ceases. The methyl-heptenols yield the corresponding saturated alcohols; the dehydration and ketonic fission which occur at ordinary pressures with nickel and platinum, respectively, are thus avoided. [Escourrou, *Chim. et Ind.*, 1925, 14, 519. See also Escourrou, *Parfums de France*, 1925, No. 26, 86.]

2405. Citronellal to dihydrocitronellal. No reduction of the aldehyde group was observed. [Sabetay and Bléger, *Bull. Soc. Chim.*, 1928 (iv), 43, 839.]

2405A. Citronellal to dihydrocitronellol (γ - η -dimethyloctanol). Nickel catalyst. [Rupe and Rinderknecht, *Helv. Chim. Acta*, 1924, 7, 541.] See para. 2353A for work by Suzuki on hydrogenation of citronellal.

¹ Adams and Garvey, *J. Amer. Chem. Soc.*, 1928, 48, 477.

² *Brit. Chem. Abst.*, 1928, 500A.

2406. Piperonal to piperonyl alcohol (m.p. 54°). Liquid phase : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **154**, 359.]

2406A. Piperonal to piperonyl alcohol with Adams-Voorhees platinum-oxide catalyst. See under Benzaldehyde, para. 1900.]

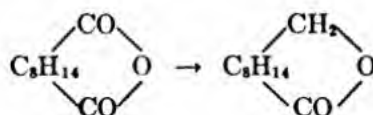
2407. Piperonal to piperonyl alcohol. Decalin solution : nickel catalyst. [Braun and Wirz, *Ber.*, 1927, **60B**, 102.]

2408. Camphene-2-carboxylic acid to dihydrocamphene-2-carboxylic acid. Glacial acetic acid solution : palladium-black.

2409. 6-Chloro-camphane-2-carboxylic acid amide to camphane-2-carboxylic acid amide (hydropinene-carboxylic acid amide). Glacial acetic acid solution : palladium-black. [Houben and Pfankuch, *Ber.*, 1926, **59B**, 2285.]

2410. Dihydrocamphene-1-carboxylic acid. See *Ibid.*, 960.

2411. Camphoric anhydride to campholid. Gas phase : nickel catalyst.



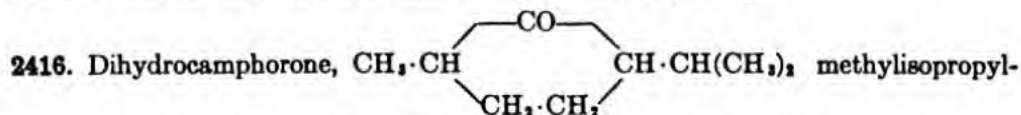
[Eijkman, *Chem. Weekblad.*, **4**, 191.]

2412. Campholanic Acid. The *cis*-acid was prepared by the reduction of campholenic acid with hydrogen and platinum-black. [Lipp, *Ber.*, 1922, **55**, 1883.] It was distilled at 140/1 mm.

2413. The *trans*-acid was obtained by reducing campholenamide in the same way (*ibid.*) and hydrolyzing the campholanamide first formed by boiling for fifty hours with 3 g. of potassium hydroxide in 15 cc. of alcohol. [Goss and Ingold, *J. Chem. Soc.*, 1925, **127**, 2780.]

2414. Ethyl- β -camphorylidenepropionate to ethyl-camphorylpropionate. Nickel catalyst. [Rupe and Tschopp, *Helv. Chim. Acta*, 1925, **8**, 351.]

2415. Camphorone to dihydrocamphorone, b.p. 182° . Gas phase : 130° : nickel catalyst. [Godchot and Taboury, *Compt. rend.*, 1913, **156**, 460.]



cyclopentane. Gas phase : 130° C. : active nickel catalyst. [Godchot and Taboury, *Compt. rend.*, 1913, **156**, 470.]

2417. Carone hydrogenated in acetic acid solution in presence of gum arabic protected colloidal platinum (germ method), under hydrogen pressure of 2 atmospheres, gave, after absorption equivalent to 1 molecule of hydrogen, *p*-menthan-2-one.

2418. On continuing until 2 molecules had been absorbed, the products were : *p*-menthane (small quantity), *p*-menthan-2-ol, and *l-p*-menthane-2 : 8-diol. [Iyer and Simonsen, *J. Chem. Soc.*, 1926, **129**, 2049.]

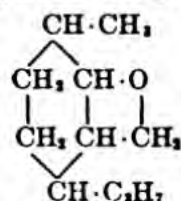
2419. Carvone to tetrahydrocarvone. Liquid phase : colloidal palladium catalyst. [Sabatier: *Catalysis*, **552**.]

2420. With 20 per cent platinum-black carvone hydrogenates successively to carvotanacetone, tetrahydrocarvone and finally carvomenthol. [Vavon, *Compt. rend.*, 1911, **153**, 68.]

2421. By Ipatiev's method, with "nickel oxide" catalyst at 280° and 120–130 atmospheres, carvone is hydrogenated to carvomenthone. [Sabatier: *Catalysis*, **591**.]

2422. In the gas phase (160° – 180°) over nickel, carvone forms a mixture of hydrocarvols. [Haller and Martine, *Compt. rend.*, 1905, **140**, 1302.]

2423. Hydroxymethylenetetrahydrocarvone gives the oxide:



on hydrogenation in alcohol solution with a nickel catalyst. [Rupe and Schäfer, *Helv. Chim. Acta*, 1928, **11**, 463; *Brit. Chem. Abst.*, 1928, 645A.]

2424. Eucarvone is hydrogenated with colloidal palladium catalyst. Wallach, *Annalen*, 1904, **336**, 37.

2425. $\text{C}_{10}\text{H}_{14}\text{O}$ (from pernitrosoketocineol) to an alcohol $\text{C}_{10}\text{H}_{20}\text{O}$. Ether solution : platinum-black catalyst. [D'Ambrosio, *Gazz. chim. ital.*, 1927, 717; *Chem. Abst.*, 1928, **22**, 774].

2426. α and β Ionones, in aqueous alcohol solution, at 1 atmosphere plus pressure with colloidal palladium catalyst with gum arabic, give first the dihydroionones (cedar smell) and then the tetrahydroionones. [Skita, Meyer and Bergen, *Ber.*, 1912, **45**, 3312. See para. 2355A for partial hydrogenation as means of improving ionones.]

2427. Desoxy- α -kessylene ketone to desoxy- α -kessylanone. Palladium catalyst. [Asahina and Nakanishi, *J. Pharm. Soc., Japan*, 1927, **544**, 485; *Chem. Abst.*, 1927, **21**, 3361; see also: *Chem. Abst.*, 1928, **22**, 1767.] This is a product from *Valeriana officinalis*.

2428. Menthone to *d*-neomenthol. Platinum-black catalyst. [Vavon and Couderc, *Compt. rend.*, 1924, **179**, 405.]

2429. According to Pickard and Littlebury [*J. Chem. Soc.*, 1912, **101**, 109], menthone (semicarbazone), on reduction by the method of Sabatier and Senderens, gives a mixture of menthol (m.p. 34°) and *neo*-menthol (m.p. 51°).

2430. *l*-Menthone to menthol. Fifty per cent alcohol : platinum-black catalyst. [Vavon, *Compt. rend.*, 1912, **155**, 287.]

2431. Schall and Kirst. Cathodic Reduction of Ketones. [*Z. Elektrochem.*, 1923, **29**, 537-546.] Study of electrolytic reduction of *l*-menthone with production of *l*-menthol, menthane, pinacol, hexahydrocymene, mercury dimethyl, according to nature of cathode.

2432. Naringenin, 2, 4, 6-trioxychalcone, to phloretin. Alcohol solution : palladium catalyst. [Rosenmund and Rosenmund, *Ber.*, 1928, **61B**, 2612.]

2433. Chalcones to hydrochalcones. Ethanol solution : palladium-black catalyst. [Bargellini and Monti, *Gazz. chim. ital.*, 1914, **44**, II, 25.]

2434. A number of catalytic reductions of chalcones to hydrochalcones and of these, by non-catalytic methods, to hydrochalcals, are reported by Pfeiffer, Kalckbrenner, Kunze and Levin, *J. prakt. Chem.*, 1928, **119**, 109.

2435. *o*-Hydroxystyryl phenyl ketone to β -*o*-hydroxyphenylethyl phenyl ketone. Platinum-black catalyst. [Marui, *Sci. Papers Tôhoku Imp. Univ.*, 1928, **17**, 695.] This is part of a research on the relation of constitution to pungency. The product of this hydrogenation is sweet and pungent.

2436. Ngaione (from *Myoporum laetum*, the "*ngaio*") to tetrahydrongaione. Ten per cent suspension in 50 per cent ethyl alcohol : Paal's colloidal palladium catalyst : $1\frac{1}{2}$ atmospheres pressure.

2437. Ngaiol (an alcohol obtained by reduction of ngaione) to dihydrongaïol, treated in the same way, the operation being suspended when 1 molecular equivalent of hydrogen had been absorbed. When for Paal's colloidal palladium, Skita's colloidal palladium or platinum was substituted a glycol, $\text{C}_{18}\text{H}_{30}(\text{OH})_2$, was obtained in considerable proportion. This may have been due to the slight acidity of Skita's preparation.

2438. Tetrahydrongaïene dioxide took up hydrogen slowly yielding $\text{C}_{18}\text{H}_{32}\text{O}_2$.³

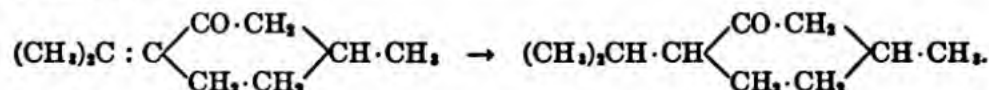
³ McDowall, *J. Chem. Soc.*, Apr. 1927, p. 731.

2439. When, in hydrogenation of ngaiol, platinum-black catalyst and acetic acid solution are used an oxido-glycol, $C_{15}H_{28}O(OH)_2$ is obtained, which is not the same as the product obtained with Skita's catalyst (para. 2437). [*Idem, Ibid.*, 1928, 1324.]

2440. Catalytic Reduction of *dl*-Piperitone. Carefully purified *dl*-piperitone was hydrogenated at the ordinary temperature, under a pressure of 0.25 atmosphere, in presence of colloidal palladium. The mixed yields from four operations, when systematically distilled under diminished pressure, gave a main fraction, b.p. 90° – $93^{\circ}/18$ mm., n_D^{20} 1.4580; this was optically inactive and appeared to be practically identical with a product which consisted of *dl*-isomenthone. Upon reducing 18 g. of the preceding product with sodium and alcohol, a yield of 15.5 g. of crude menthol was obtained. *dl*-isomenthone prepared by the catalytic reduction of *dl*-piperitone gave a similar product, which, however, furnished a considerably higher proportion of the crystalline oxime. [Read and Cook, *J. Chem. Soc.*, 1925, 127, 2786.]

2441. *l*-Piperitone to *d*-iso-menthone. *d*-Piperitone to *l*-iso-menthone. *d*-Pulegone and *l*- Δ^4 -*p*-menthen-3-one to mixtures of *d*-iso-menthone and *l*-menthone. [Read and Robertson, *J. Chem. Soc.*, 1926, 2209.]

2442. Pulegone (b.p. 221°) to pulegomenthone. Gas phase : 140° – 160° : nickel : brisk current of hydrogen : 25–35 g. per hour; 5 g. nickel-pumice. Conditions essential to prevent tar formation.



[Haller and Martine, *Compt. rend.*, 1905, 140, 1298.]

2443. Apparently, hydrogenation in alcoholic solution with platinum-black catalyst gives the same product. [Vavon, *Compt. rend.*, 1912, 155, 287.]

2444. *d*-Pulegone to *d*-isomenthone and *l*-menthone. Likewise *l*- Δ^4 -*p*-menthen-3-one. [Read and Robertson, *J. Chem. Soc.*, 1926, 2209; *C. A.*, 1927, 21, 78.]

2445. Benzylidenepulegone to benzylmenthone. Solution in 82 per cent ethanol : nickel catalyst : 90 per cent yield. [Rupe and Schäfer, *Helv. Chim. Acta*, 1928, 11, 463.]

2446. Tagetone (η -methyl- γ -methylene- $\Delta\alpha$ -octen- ϵ -one) to γ , η -dimethyloctan- ϵ -one by catalytic hydrogenation. Gas phase : 180° : nickel-pumice catalyst. Also in ether solution with platinum black. [Jones and Smith, *J. Chem. Soc.*, 1925, 27, 2530.]

2447. $\gamma\eta$ -Dimethyl- $\Delta\alpha$ -octen- ϵ -one was similarly reduced to $\gamma\eta$ -dimethyloctan- ϵ -one. [*Ibid.*]

2448. Thujone and isothujone with colloidal palladium catalyst, at 2 atmospheres pressure add H_2 . [Wallach, *Annalen*, 1904, 336, 37.]

2449. Thymoquinone [$(CH_3)(C_6H_5)(1, 4)C_6H_3(2, 5)O_2$] to corresponding diphenol. Gas phase at 200° C. Nickel catalyst. [Sabatier: *Catalysis*, 442.]

2450. Zingerone: hydrogenation of condensation products. Zingerone (0-4-hydroxy-3-methoxyphenylethyl methyl ketone) condensed with *n*-butyraldehyde gives β -4-hydroxy-3-methoxyphenylethyl *n*-pentenyl ketone and this on catalytic reduction with platinum-black yields β -4-hydroxy-3-methoxyphenylethyl *n*-pentyl ketone. With *n*-valeraldehyde the product is β -4-methoxyphenylethyl *n*-hexenyl ketone, which also undergoes hydrogenation to the saturated ketone. [Nomura and Choi, *Sci. Rep. Tōhoku Imp. Univ.*, 1928, 17, 707.]

CHAPTER XXV

HYDROGENATIONS AT NITROGEN LINKAGES

I

NITRITES AND NITRO COMPOUNDS

2500. Methyl Nitrite to Methylamines. In the gas phase at 180° C. over a nickel catalyst methyl nitrite yields a mixture of amines with the secondary amine predominating. [Gaudion, *Ann. Chim. Phys.*, 1912 (8), **25**, 129.]¹

2501. Propyl nitrite to a mixture of amines, propyl-amine, dipropyl-amine and tripropyl-amine, the secondary amine in largest yield. Gas phase : 200° : nickel catalyst. [Gaudion, *Ann. Chim. Phys.*, 1912 (8), **25**, 129.]

2502. Isopropyl nitrite, at 200° over nickel, gives a mixture of isopropyl-amines, the secondary amine predominating. [Gaudion, *Ann. Chim. Phys.*, 1912, (8), **25**, 129.]

2503. Isobutyl nitrite at 220° over nickel gives a mixture of the isoamyl-amines, the di-isoamyl-amine being formed in largest quantity. [Gaudion, *Ann. Chim. Phys.*, 1912 (8), **25**, 129.]

2504. Isoamyl nitrite over nickel at 220° gives 31 per cent mono-, 62 per cent di-, and 7 per cent tri-iso-amyl-amine. [Gaudion, *Ann. Chim. Phys.*, 1912 (8), **25**, 129.]

2505. Special Nickel Catalyst for the Catalytic Reduction of Organic Nitro-compounds. For the preparation of a nickel catalyst, dust-free air is passed for four hours at 70° through aqueous nickel nitrate solution containing 25 per cent ammonia and finely divided silica gel, the precipitate being dried and reduced in hydrogen first at 100°–130° and then at 550°; the catalyst is finally cooled in hydrogen or nitrogen and transferred to the liquid (water, pyridine, decalin) for use. The precipitate obtained by adding nickel nitrate solution at 70° dropwise to a very dilute sodium carbonate solution may be similarly worked up. These catalysts are used in the reduction of various nitro-compounds with hydrogen at 60°–100° to give amines and diamines, namely, α -naphthylamine, *m*- and *p*-phenylenediamines, cresidine, *o*-chloroaniline, 4-chloro- α -naphthylamine (m.p. 95°), aniline-*o*-sulphonic acid, *o*-aminoacetanilide (m.p. 120°–121°) hydrochloride, (m.p. 132°), *p*-aminoacetanilide, *p*-aminobenzoic acid, ethyl 3-amino-4-hydroxybenzoate, naphthostyryl and 5-amino-1-naphthoic acid (from 1 : 5[8]-nitronaphthoic acid), 2 : 5-dichloroaniline (m.p. 50°), 2 : 4 : 6-triaminotriphenyl-1 : 3 : 5-triazine, 5-amino-acenaphthene, methyl 5-m-nitrobenzoylsalicylate (m.p. 130°–131°) 3-amino-*p*-tolyl carbonate (m.p. 146°–147°), 4-chloro-2-aminophenol; benzeneazosalicylic acid gives 5-aminosalicylic acid, and azoxybenzene yields aniline. Reduction of nitrites under these conditions gives a larger proportion of primary and less secondary amine. From phenylacetonitrile are obtained 63 per cent of β -phenylethylamine and 18 per cent of secondary base; from *p*-nitrophenylacetonitrile *p*-aminophenylacetonitrile and β -*p*-aminophenylethylamine, b.p. about 147°–11 mm., result at 50° and 90°, respectively. Similarly α -naphtho-nitrile gives (1-naphthylmethyl)amine (70 per cent) and

¹ See: Davis and Elderfield. The catalytic preparation of methylamine from methyl alcohol and ammonia, *Publ. Mass. Inst. Tech.*, 1928, **64**, No. 37.

di-(1-naphthylmethyl)amine (20 per cent), acetonitrile ethylamine, and propionitrile *n*-propylamine (80 per cent). Other reductions described are: crotonaldehyde to *n*-butyl alcohol; cinnamionitrile to β -phenylpropionitrile and thence to γ -phenyl-*n*-butylamine; acetophenone to phenylmethylcarbinol and thence to ethylbenzene; diethyl ketone to diethylcarbinol (γ -hydroxypentane); ethyl acetoacetate to ethyl γ -hydroxy-butyrate; 2-*p*-toluoylbenzoic acid to 4-methyldiphenyl-methane-2'-carboxylic acid, and the nitro-compound to 3-amino-4-methyldiphenylmethane-2'-carboxylic acid, m.p. 130°-136°; benzophenone to diphenylmethane, b.p. 260°-262°; *m*-nitro-*p*-tolyl sulfo- α -naphthyl ketone to *m*-amino-*p*-tolylsulpho-1-naphthylmethane; 2 : 2'-di-nitrodi-*p*-anisyl ketone to 2 : 2'-diaminodi-*p*-anisylmethane, m.p. 110°; phenyl *m*-nitro-*p*-tolyl ketone to 3-amino-4-methyldiphenylmethane (hydrochloride, m.p. 218°); 3-nitro-di-*p*-tolylketone to 3-aminodi-*p*-tolylmethane (hydrochloride, m.p. 210°-211°); acetoxime to isopropylamine; quinaldine to tetrahydroquinaldine at 80°, or decahydroquinaldine at 130°; pyridines to piperidines.²

2506. Catalytic Activity of Tin in Reduction of Nitro-compounds.³ Tin is a good catalyst for the reduction of nitrobenzene, *o*-nitrotoluene, and *o*-nitroanisole by hydrogen. Of all the forms of tin catalyst investigated, that made from stannous hydroxide, prepared by the action of sodium carbonate on a solution of stannous chloride, is the most efficient. Oxidation of the hydroxide, prior to reduction to the metal, increased the efficiency of the resulting catalyst; the lower the temperature of oxidation, within the limits examined (150°-300°), the better the resulting catalyst. The lower the temperature of reduction of the oxide, within the limits of the experiments, likewise the better the resulting catalyst. A tin catalyst in the form of coarse lumps is better than the powdered form. The behavior of the catalyst in iron and glass tubes is very different, a higher temperature being necessary in glass tubes than in iron for the same results. Tin permits of a larger variation of temperature than many other catalysts. Probably 275°-294° is the best temperature for the production of aniline when a glass tube is used. The best rates of flow of nitrobenzene and hydrogen with the tin catalyst compare closely with those for a copper catalyst. When *o*-nitrotoluene and *o*-nitroanisole were used instead of nitrobenzene, yields of 94 per cent and 93 per cent were obtained of *o*-toluidine and *o*-anisidine respectively. Experiments carried out in a larger apparatus gave yields of 99 per cent of aniline and 98-99 per cent of *o*-toluidine.⁴

2507. Titania Catalyst for Reduction of Nitro-compounds in the Vapor Phase.⁵ The work was done on nitrobenzene. Titanium hydroxide precipitated by ammonia from a boiling 2.25 per cent aqueous solution of titanium trichloride, was dried at 100° C. and reduced in hydrogen at 302° C. This produced a catalyst which gave a minimum of by-products when used at 282° C. The best yields were obtained with a hydrogen flow of 14 liters an hour and a nitrobenzene flow of 4.05 $\frac{1}{2}$., over 14 g. of catalyst. The addition of 5 per cent of manganese improved the color of the product. Ignited catalysts gave by-products.

2507A. Busch and Schulz effect the hydrogenation of nitro compounds by boiling them in alcoholic 5 per cent potassium hydroxide, the hydrogen being furnished by the decomposition of hydrazine hydrate in presence of palladized calcium carbonate. The reaction goes better in methanol than in ethanol. Thus, nitrobenzene in ethanol yields azoxybenzene, in methanol it gives azobenzene. By increasing the quantity of catalyst hydrazobenzene and, ultimately, aniline are obtained. The method has been applied to nitrophenols, to *m*-nitrobenzenesulphonic acid, to nitranilines and to many other nitro-aromatic compounds. [*Ber.* 1929, 62B, 1458; *Brit. Chem. Abst.*, 1929, 923A.]

2508. Nitromethane to methyl-amine. Gas phase : 150°-180° : nickel catalyst : no

² French Pat. 621,434, July 20, 1926; Ger. Pat., July 22, 1925; additional to Brit. Pat. 255,884, to the I. G.; *Brit. Chem. Abst.*, 1928, 361B.

³ Brown and Henke, *J. Phys. Chem.*, 1923, 27, 52, 739.

⁴ *J. Chem. Soc., Abst.* 1923, i, 201.

⁵ Fzel, *J. Phys. Chem.*, 1928, 32, 852; *Chem. Abst.*, 1928, 23, 3338.

side reactions. Between 200° and 300°, methane, ammonia, dimethyl-amine and trimethyl-amine are also produced.

2509. Over copper between 300° and 400° (no reduction below 300° C.) or, more slowly, over platinum sponge at 300°, nitromethane is hydrogenated to methyl-amine, but with the production of a foul-smelling liquid, which deposits crystals of the methyl-amine salt of nitromethane. [Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 226.]

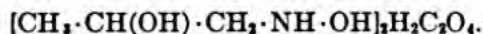
2510. Nitromethane and Aliphatic Nitro Alcohols to Hydroxylamines. The conditions under which aliphatic nitro-alcohols can be reduced to the corresponding hydroxylamines without simultaneous formation of the amines have been determined. The success of the method appears to depend on the maintenance of a suitable hydrogen-ion concentration in the solution.

Reduction is effected with hydrogen in the presence of palladized barium sulphate. Nitromethane and α -nitropropan- β -ol in aqueous solution in the presence of oxalic acid give hydroxylaminomethane oxalate $(\text{NHCH}_2\cdot\text{OH})_2\text{C}_2\text{H}_2\text{O}_4$, m.p. 158° (decomp.), and α -hydroxylaminopropan- β -ol oxalate, m.p. 111° (decomp.). In 96 per cent alcoholic solution, α -nitrobutan- β -ol and α -nitropentan- β -ol similarly afford α -hydroxylaminobutan- β -ol oxalate, m.p. 100°–101° (decomp.), and α -hydroxylaminopentan- β -ol oxalate, m.p. 99° (decomp.), whereas for the production of α -hydroxylamino- n -methylpentan- β -ol oxalate (decomp. 144°–145°), the addition of acetic acid is necessary. α -Nitro- γ -methylbutan- β -ol is hydrogenated in aqueous alcoholic solution in the presence of oxalic acid to α -hydroxylamino- γ -methylbutan- β -ol oxalate (m.p. 106°–108° (decomp.)), whereas the production of α -hydroxylamino-octan- β -ol oxalate, decomp. 142°–143°, requires the simultaneous presence of acetic acid. [Schmidt, Ascherl and Mayer, *Ber.*, 1925, **58**, 2430, *Brit. Chem. Abst.*, 1926, 45A.]

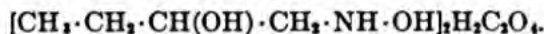
2511. Nitromethane and aliphatic nitro-alcohols, hydrogenated with palladium (5 per cent) on barium sulphate: aqueous solution. [See Traube and Schulz, *Ber.*, 1923, **56**, 1860.]

2511A. Example: Nitromethane 6.1 g., oxalic acid crystals 6.3 g., water 77 cc., catalyst 1 g., hydrogen 100 cc., gives hydroxylaminomethane oxalate $(\text{CH}_2\cdot\text{NH}\cdot\text{OH})_2\text{H}_2\text{C}_2\text{O}_4$.

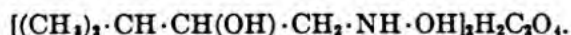
2511B. Nitropropanol gives 1-hydroxylamino-propanol-2-oxalate,



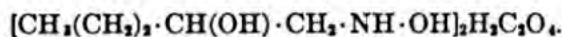
2511C. Nitrobutanol (2) gives 1-hydroxylamino-butanol-2-oxalate,



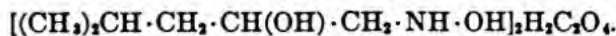
2511D. 4-Nitro-2-methyl-butanol-3 gives 4-hydroxylamino-2-methyl-butanol-3-oxalate



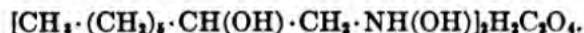
2511E. 1-Nitropentanol-2 gives 1-hydroxylamino-pentanol-2-oxalate



2511F. 5-Nitro-2-methyl-pentanol-4 gives 5-hydroxylamino-2-methyl-4-pentanol-oxalate,



2511G. 1-Nitro-octanol-2 gives 1-hydroxylamino-octanol-2-oxalate,



[Schmidt, Ascherl and Mayer, *Ber.*, 1925, **58**, 2430.]

2512. Nitroethane to ethyl-amine (with diethyl-amine, triethyl-amine and ammonia). Gas phase : 200° : nickel catalyst. Above 350° some ethane and methane are produced. [Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 227.]

2513. With a copper catalyst at 300°–400° nitroethane is hydrogenated easily to ethyl-amine. (*Ibid.*)

2514. Nitropyruvic ureide $\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}:\text{CHNO}_2$ to the oxime of hydantoin-5-aldehyde $\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{NOH}$ with Voorhees-Adams catalyst. 9.3 g.

ureide suspended in 100 cc. glacial acetic acid : 0.1 g. catalyst : atmospheric pressure : forty-five minutes. [Davidson, *J. Am. Chem. Soc.*, 1925, **47**, 1722.]

2515. Aromatic Nitro-compounds to Amines. Various solvents, especially ethanol, ethyl acetate and acetone. Adams platinum-black catalyst.

2515A. *m*-Nitrobenzalacetophenone to *m*-aminobenzalacetophenone.

2515B. *m*-Nitrobenzylacetophenone to *m*-aminobenzylacetophenone.

2515C. *m*-Nitrobenzalacetone to *m*-aminobenzalacetone.

2515D. *m*-Nitrobenzylacetone to *m*-aminobenzyl acetone.⁶

2516. Nitrobenzene (0.1 mol.) in absolute alcohol (150 cc.) is reduced quantitatively to aniline in ten to eleven minutes by hydrogen at 2–3 atmospheres pressure in presence of 0.2 g. of platinum-black prepared by reduction of platinum oxide. Replacement of a portion of the alcohol by water decreases the rate of reduction. The rate of reduction in methyl and *n*-propyl alcohols is the same as that in ethyl alcohol, but is progressively less in *n*-butyl and isoamyl alcohols. Ethyl acetate and acetone are as satisfactory solvents as is 95 per cent alcohol, but the reduction is much slower in dry ether and still slower in glacial acetic acid. All the nitro-toluenes and nitrobenzoic acids, *o*- and *p*-chloronitro-benzenes, *p*-nitroanisole, and *p*-nitrophenetole are reduced under the above conditions at approximately the same rate as nitrobenzene, while the methyl nitrobenzoates and 1-nitronaphthalene are reduced more rapidly. Exhaustive reduction of the above chloronitrobenzenes under these conditions yielded some cyclohexylamine hydrochloride. Addition of hydrochloric and acetic acids decreases the rate of reduction, while this is completely inhibited by the addition of 0.025 mol. of sodium hydroxide in saturated aqueous solution, or by 0.0005 mol. of zinc acetate. Under the above conditions, *m*-nitrostyryl methyl ketone, phenyl *m*-nitrostyryl ketone, and ethyl *m*-nitrocinnamate undergo reduction only at the nitro-group. Addition of acetic acid retards the reaction, but this proceeds until the ethylene linking is also reduced. In the case of a mixture of nitrobenzene and safrole, the former is reduced first, and no reduction takes place in presence of sodium hydroxide. Addition of the latter does not, however, inhibit reduction of safrole alone, indicating the probable formation of a non-reducible compound between the nitrobenzene and the sodium hydroxide. The inhibition of the reduction of nitrobenzene by zinc acetate is partly prevented if safrole is also present.⁶

2517. In manufacturing aromatic amines, a catalytic mass obtained from copper salts with the addition of salts or oxides of other heavy metals (iron, silver, zinc) may be used. The reduction of copper salts is effected before or after the addition of the heavy metal compounds. [*Chem. Abst.*, 1915, **9**, 2569.]⁷

2518. In catalytic hydrogenations, especially the reduction of aromatic nitro compounds to amines, the hydrogen may be wholly or partly replaced by a mixture of carbon monoxide and steam. For example, aniline can be prepared by passing a mixture of nitrobenzene and gas, containing carbon monoxide and steam, over a copper catalyst produced by coating pumice with a mixture of copper carbonate, zinc carbonate, and sodium silicate and reducing.⁸

2519. Aromatic Amines: Preparation of. Aromatic nitro-compounds are reduced by hydrogen or a mixture of hydrogen with other gases e.g., with carbon dioxide or with gases containing carbon dioxide, in presence of water and a catalyst, under high pressure and at a temperature above the boiling-point of the amine produced. Iron turnings may

⁶ Adams, Cohen and Rees, *J. Amer. Chem. Soc.*, 1927, **49**, 1093.

⁷ Ger. Pat. 283,449, Mar. 6, 1914 (addition to 282,568), to the Badische Company.

⁸ Brit. Pat. 6409, Apr. 29, 1915, to the Badische Co.; *Chem. Abst.*, 1916, **10**, 2971.

be used as catalyst. The process may be made continuous by providing a loaded valve for the escape of the amine vapor.⁹ [*J.S.C.I.*, 1915, **34**, 943.]

2520. Sulphides for Nitro Reduction. Since sodium or ammonium polysulphides and thiosulphates are reduced to sulphides, especially in presence of silica gel, heavy metal oxides, etc., by hydrogen or carbon monoxide at high pressures (100–200 atmospheres) and temperatures (150°–180°), a small amount of sulphide is sufficient in the presence of these gases under these conditions to reduce a large quantity of aromatic nitro-compound. The sulphide may be replaced by caustic alkali (or ammonia) and sulphur, or by polysulphides or thiosulphates. Part of the thiosulphate formed (or introduced) is converted at the temperatures used into sulphate; by employing 1.7–5 per cent of the ammonium sulphide theoretically required there is obtained at the end of the reduction ammonium sulphate free from sulphide or thiosulphate. The hydrogen and carbon monoxide need not be purified.¹⁰

2521. Herold and Koppe¹¹ obtain primary aromatic amines by treating the corresponding nitro-compounds with hydrogen or carbon monoxide, or both, at 100° C., or higher, under 100 atmospheres pressure, in the presence of soluble sulphides in quantity insufficient for the complete reduction.

2522. Aromatic nitro-compounds are reduced to amines by hydrogen under 140–200 atmospheres pressure in presence of a metal catalyst (iron powder, spongy iron, nickel deposited on zeolite). Catalyst poisons (e.g., sulphur) must be present in the nitro-compound, or the reducing gas to diminish the activity of the catalyst. Reaction begins at about 100°; 150°–200° is recommended.¹²

2523. Aromatic nitro-compounds are treated with gases containing hydrogen sulphide (e.g., crude coal gas), preferably admixed with a basic substance such as ammonia, by passing simultaneously through a layer of porous animal or vegetable charcoal (*cf.* Ger. Pat. 290,656). The nitro-compound is reduced to the amine with evolution of heat, the sulphur formed being deposited within the pores of the carbon. The carbon loses its activity when it has absorbed about its own weight of sulphur, but can be reactivated by removing the sulphur either by melting, heating, or extraction with a solvent. The rate of reduction is greatly increased by the presence of a small percentage of basic substance. Thus, nitrobenzene vapor is reduced to aniline by a gas containing 10 g. of hydrogen sulphide and 0.5 g. of ammonia per cubic meter.¹³

2524. Preparation of Primary Aromatic Amines. In the catalytic reduction of technical aromatic nitro-compounds, the effect of catalyst poisons is avoided by adding to the catalyst an alkaline earth metal, aluminum, rare earths, or compounds of these. An activator, such as chromium oxide, manganese oxide, alkali, or alkali silicate, is usually also added. Thus, dry copper carbonate is ground with calcium oxide to a fine powder, pasted on pumice with sodium silicate solution, and reduced at 220°–230° to form a catalyst suitable for reduction of crude nitrobenzene vapor at 200°. Technical *o*-nitrotoluene and 3 nitro-*o*-xylene may similarly be used.¹⁴

2525. Reduction of Organic Nitro-compounds. Kahn and Mayer¹⁵ silica-gel impregnated with copper (or other suitable heavy metal such as nickel) is used as catalyst in hydrogenation of nitro-compounds in the vapor phase. Examples given are:

⁹ Ger. Pat. 281,100, Feb. 6, 1914, to von Girssewald.

¹⁰ *Brit. Chem. Abst.*, **1928**, 780; Brit. Pat. 295,824, Aug. 4, 1927, to Johnson as agent of I. G. Farbenind. A.-G.; French Pat. 639,557, Aug. 16, 1927, to I. G.; Ger. Pat. 467,638, Jan. 1, 1927, to I. G. (Herold named as inventor.)

¹¹ U. S. Pat. 1,662,421, Mar. 13, 1928.

¹² *Brit. Chem. Abst.*, **1928**, 846B; Brit. Pat. 297,212, Nov. 10, 1927, to Johnson as agent of I. G. Farbenind. A.-G.

¹³ Ger. Pat. 388,185, 1921, to Bayer Co. and Engelhardt; *J. S. C. I.*, **1924**, 808B, from *Chem. Zentr.*, 1924, ii, 545.

¹⁴ *Brit. Chem. Abst.*, **1927**, 579B. Ger. Pat. 436,820, Jan. 12, 1924, to I. G. Farbenind. A.-G. assignees of Schmidt and Feller.

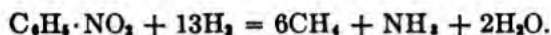
¹⁵ U. S. Pat. 1,639,186, Aug. 16, 1927, assigned to Grasselli Dyestuff Corp.

Nitrobenzene to aniline at 200° C. The nitrotoluenes to the corresponding toluidines at 220°–225° C. Alpha-nitronaphthalene to alpha-naphthylamine, with superheated steam and hydrogen at 240° C. 3-nitropyridine to 3-aminopyridine at 200°–250° C. Nitromethane to methylamine at 180° C.

2526. Nitro-compounds are reduced, in the presence of a catalyst, by gases containing carbon monoxide, but kept free from metal carbonyls, particularly iron carbonyl, by excluding iron from the inner surface of the contact chamber and from the inlet pipe, by coppering these or otherwise. For example, over a contact mass at 180°–250°, is led a mixture of nitrobenzene vapor and water-gas, the latter having been desulphurized in the usual way and then freed from metal carbonyls by leading over activated charcoal. The contact mass remains active for a long time. The yield of aniline is quantitative. Water and carbon dioxide are also formed, and after absorption of the latter, the gases leaving the contact chamber can be used again. The moist aniline, after distillation, is obtained quite pure. Nitro-compounds can be reduced in gaseous condition or as liquids in solution, with or without application of pressure.¹⁶

2527. Nitrobenzene. In gas phase. Over nickel of limited activity, at 200°, the vapors of nitrobenzene are hydrogenated to aniline. But above that temperature, or with fully active nickel, the aromatic nucleus is hydrogenated and more or less cyclohexylamine is produced. [Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 226.]

2527A. Above 250°, benzene and ammonia are formed, and, above 300°, the benzene nucleus breaks up with the production of methane:



2527B. A German Patent 139,457, of July 26, 1901, to J. B. Senderens, is probably the first patent record having to do with the reduction of organic bodies by hydrogen in the presence of nickel catalyst. This patent is for the production of aniline from nitrobenzol and involves passing the latter body in the form of a vapor over heated nickel, copper, cobalt, iron or palladium in the presence of hydrogen. The hydrogen may be in the pure state or in the form of water-gas.

2528. Aniline may be made by passing the vapors of nitrobenzene, with hydrogen and steam, at 120°, over catalytic nickel. The yield is said to be quantitative.¹⁷

2529. According to Sabatier and Senderens, copper is the best catalyst for the hydrogenation of nitrobenzene to aniline, in the gas phase, because it does not cause hydrogenation of the aromatic nucleus. The reaction commences at 230° and is rapid and regular between 300° and 400°. The hydrogen may, on the commercial scale, be replaced by water gas. The reducing gas should be in excess. The yield is about 98 per cent of aniline, with only traces of nitrobenzene and azobenzene. [Sabatier and Senderens, *Compt. rend.*, 1901, 133,321; Sabatier, *Fifth Congr. Pure and Appl. Chem.*, Berlin, 1902, II, 617; Senderens, French Pat. 312,615, 1901.]

2530. Palladium. Palladium previously charged with hydrogen was used by Graham to reduce nitrobenzene to aniline.

2531. Saytzeff showed that hydrogen acting on nitrobenzene in the presence of palladium reduced the nitrobenzene to aniline. [*J. prakt. Chem.*, 1871, (2), **4**, 418.]

2532. Platinum in various forms can catalyze the hydrogenation of nitrobenzene to aniline, but the activity is slight and, unless the hydrogen is in large excess, hydrazobenzene is formed. [Sabatier and Senderens, *Ann. Chim. Phys.*, 1905 (8), **4**, 414.]

2533. By passing vapors of nitrobenzene and methanol (the latter in excess) over thorium at 420°, aniline is produced. The reduction is due to the products (2H₂ and CO) of the decomposition of the methanol. [Sabatier and Murat, *Compt. rend.*, 1913, **157**, 1499; *Bull. Soc. Chim.*, 1914 (4), **15**, 227.]

2534. Nitrobenzene to aniline in the vapor phase. [Sermeria and Milone, *Atti*

¹⁶ *Brit. Chem. Abst.*, **1926**, 870B; Ger. Pat. 429,102, Aug. 29, 1924, to I. G. Farbenind. A.-G., assignees of Schmidt and Johanssen.

¹⁷ Ger. Pat. 282,492, 1913, to Meister, Lucius and Brünig.

accad. sci. Torino, 1927-1928, **63**, parts 1-3; *Chem. Abst.*, 1928, **22**, 2098. A study of the hydrogenation of nitrobenzene over copper and silver on pumice.

2535. The reduction of nitrobenzene vapor to aniline by means of hydrogen in presence of coppered or silvered asbestos is exothermic, and the best yield is obtained at temperatures not exceeding 350° C. with copper and at 400° C. with silver. The yield at first increases rapidly and then remains constant. The influence of increase of the amount of hydrogen used on the yield becomes larger as the temperature is raised and as the catalyst is increased in quantity. The yield is not changed much by variation in the hourly supply of nitrobenzene. The catalyst retains its initial activity for months. The aniline obtained in presence of copper is always slightly colored by the presence of traces of nitrobenzene, but the silver catalyst gives pure aniline in quantitative yield. [Serneria and Milone, *Annali Chim. Appl.*, 1928, **18**, 58; *Brit. Chem. Abst.*, 1928, 327B.]

2536. Liquid Phase. On prolonged contact between an alcoholic solution of nitrobenzene and excess of hydrogen in presence of palladium-black, aniline is eventually formed. [Gerum, *Inaug. Diss.*, Erlangen, 1908.]

2537. Brown, Etzel and Henke studied the hydrogenation of nitrobenzene, α -nitronaphthalene, *p*-nitrotoluene, *o*-nitrophenol, *p*-nitrophenol, and dinitrotoluene with hydrogen gas at 15 to 47 atmospheres pressure. The catalyst was reduced powdered nickel oxide from the nitrate. The static or "batch" method was used. Quantitative reduction of the nitro-compounds to amines was obtained at 215° and 34 atmospheres; 0.52 g. catalyst per gram nitro-compound was the optimum catalyst ratio. Benzene and methanol were the best solvents. Ethylene glycol was a poorer solvent.¹⁸

2538. Nitrobenzene to azobenzene. Vapor phase, 260° C. : thallium-asbestos catalyst. Other supports (aluminum hydroxide, pumice, "nonpareil brick") gave negligible yields. Unsupported thallium lost activity through sintering. [Brown, Brothers and Etzel, *J. Phys. Chem.*, 1928, **32**, 456; *Brit. Chem. Abstr.*, 488A, 1928.]

2539. Hydrogenation of Nitrobenzene in Presence of Benzaldehyde and of Piperonal.¹⁹ Catalytic hydrogenation of nitrobenzene with platinum-black in presence of benzaldehyde yields phenyl-*N*-phenylnitrone and phenylbenzylhydroxylamine, and in presence of piperonal, piperonyl-*N*-phenylnitrone, $\text{CH}_2\text{O}_2 : \text{C}_6\text{H}_5 : \text{NC}_6\text{H}_4\cdot\text{OH}$, melting-point about 135°. This confirms the view that the reduction of nitrobenzene alone proceeds through the stage of phenylhydroxylamine.²⁰

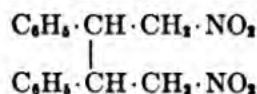
2540. Nitrotoluenes to toluidines. Gas phase 200°-250° with nickel catalyst : 300°-400° with copper catalyst. [Sabatier and Senderens, *Compt. rend.*, 1901, **133**, 321.]

p-Nitrotoluene to *p*-toluidine. Acetone or ether solution : platinum-black catalyst, 1 part platinum to 100 by weight of substrate. [Cusmano, *Lincei*, 1917, **26** (2), 87.]

2541. Ortho-nitrotoluene to orthotoluidine.²¹ Ortho-toluene is treated with a gas containing hydrogen, with a copper catalyst (reduced below 300° C.) with activators (promoters.)

2542. Similarly para-toluidine is prepared from para-nitrotoluene.²²

2543. An exception to the avidity with which a nitro group usually takes hydrogen to form an amino compound is ω -nitrostyrene, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$, which dissolved in absolute alcohol or in glacial acetic acid, in the presence of platinum-black catalyst, is hydrogenated to saturation by taking up only 1 atom of hydrogen, the nitro group being unaffected, 2 molecules of the product uniting to form:



[Sonn and Schnelleberg, *Ber.*, 1917, **50**, 1913.]

¹⁸ *J. Phys. Chem.*, 1928, **32**, 631; *Chem. Abst.*, 1928, **22**, 1891.

¹⁹ Vavon and Crajinovic, *Compt. rend.*, 1928, **187**, 420.

²⁰ *Brit. Chem. Abst.*, 1928, 1125A.

²¹ Swiss Pat. 72,691, June 16, 1916, to the Badische Co., *Chem. Abst.*, 1916, **10**, 2616.

²² Swiss Pat. 72,593, June 16, 1916, to the Badische Co., *Chem. Abst.*, 1916, **10**, 2616.

2544. By operating in presence of mineral acids, the formation of these di-molecular compounds was avoided. Thus 20 g. nitrostyrene, 0.75 g. platinum-black, 200 cc. dry methyl alcohol into which dry hydrogen chloride had been passed, were shaken with hydrogen. This yielded only 0.8 g. of dimolecular product. From the filtrate were obtained two isomeric phenylacetaldoximes. Kelber's nickel catalyst gave a similar result. [Kohler and Drake, *J. Am. Chem. Soc.*, 1923, **45**, 1281.] With platinum-black 3-methoxy-4-ethoxy- α -nitrostyrene gives 3-methoxy-4-ethoxyphenylaminoethane. [Sawai, *J. Pharm. Soc., Japan*, 1929, **49**, 260; *Chem. Abst.*, 1929, **23**, 3203.]

2545. *p*-Nitrophenylethyl chloride to hexahydro-*p*-aminophenylethyl chloride, β -[*p*-amino-cyclohexyl]-ethyl chloride. Nitro-compound 37.2 g. ($= \frac{1}{2}$ mol.), glacial acetic acid 40 cc., water 100 cc., conc. hydrochloric acid 40 cc.; colloidal platinum catalyst 20 cc. ($= 0.2$ g. platinum in gum arabic solution 1 : 10) : 50° C., 2.5 atmospheres hydrogen pressure : Skita's method and (modified) apparatus. Hydrogen absorption having slowed up, after seven and one-half hours 1.0 g. platinum (as the chloride) was added. After thirteen and three-quarter hours the hydrogen absorption was 29.29 liters against a theoretical 28.84. [Ferber, *Ber.*, 1929, **62B**, 191.]

2546. In a similar manner β -[*p*-aminocyclohexyl] ethyl alcohol, $H_2N \cdot C_6H_{10} \cdot CH_2 \cdot CH_2 \cdot OH$ was prepared from *p*-aminophenylethyl alcohol. [*Idem, Ibid.*]

2547. *o*-Nitroisopropylbenzene to *o*-amino-isopropyl benzene. Acetic acid solution : platinum-black. [Vavon and Cailler, *Bull. Soc. chim.*, 1927, **41** (iv), 357.]

2548. Mononitrocymene (1-methyl-2-nitro-4-isopropyl-benzene) to monoaminocymene (1-methyl-2-amino-4-isopropyl-benzene). Liquid phase : nickel catalyst.²³

2549. Secondary and tertiary aromatic amines to primary and secondary amines and hydrocarbons or phenols. Secondary or tertiary amines of the general formula $Aryl \cdot NRR'$ ($R = H$, alkyl or benzyl; $R' =$ benzyl or substituted benzyl) are treated with hydrogen in presence of metal catalysts. E.g., ethylbenzylaniline and alcohol are shaken with hydrogen in presence of palladium-black: toluene and ethylaniline result. Similarly methylbenzylaniline gives methylaniline and toluene; benzylaniline gives aniline and toluene; dibenzylaniline gives aniline and toluene; 3 : 4-methylene-dioxybenzylaniline gives aniline and 3 : 4-methylene dioxytoluene : ortho-hydroxybenzylaniline gives ortho-cresol and aniline.²⁴

2550. Nitrophenols to amino-phenols (with some phenol, aniline and ammonia). Gas phase 160–190° : nickel catalyst. [Mignonac, *Bull. Soc. Chim.*, 1910 (4), **7**, 270.]

2551. Copper is an excellent catalyst for the hydrogenation of the nitrophenols to amino-phenols, at 265°. [Brown and Carrick, *J. Amer. Chem. Soc.*, 1919, **41**, 436.]

2552. Graham used palladium previously charged with hydrogen, to reduce nitro phenols to amino-phenols.

2553. *p*-Aminophenol.²⁵ Phenol in alkaline solution is coupled with a diazo compound from a primary aromatic amine such as benzidine, tolidine, α - or β -naphthylamine, or "an aminosulphonic, hydroxy-sulphonic, chlorosulphonic, carbonic, chlorocarbonic, or like base." The resulting azo compound is reduced with hydrogen or other reducing gas or mixture in the presence of a catalyst. As catalysts are mentioned, finely divided metals, such as nickel, cobalt, copper, or iron and their oxides. The base is recovered by filtration, or in the case of benzidine or tolidine by addition of sodium sulphate or sulphuric acid and the *p*-aminophenol isolated from the remaining solution.²⁶

2554. Nitrosoterpenes to corresponding hydroxylamines. Acetone or ether solution : platinum-black catalyst, 1 part of platinum to 100 by weight of substrate. [Cusman *Lincei*, 1917, **26**, (2), 87.]

2555. Aromatic Dinitro-derivatives: reduction by hydrogen and platinum-black: The action is selective on one of the nitro groups. Metadinitrobenzene yields meta-

²³ U. S. Pat. 1,314,920, Sept. 2, 1919, to Andrews, assignor to The Selden Co.

²⁴ Krauss (assignor to E. Merck), Ger. Pat. 432,151, Aug. 21, 1924, addition to 407,487; *J.S.C.I. Suppl.*, 1926, 964B.

²⁵ Poma, Brit. Pat. 194,694, Mar. 1, 1923.

²⁶ *Chem. Abst.*, 1923, **17**, 3510.

nitraniline. 1 : 2, 1 : 3, 1 : 8-dinitronaphthalenes yield 2-, 3-, 8-, nitronaphthylamines respectively.

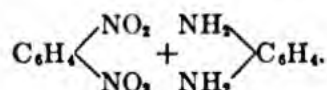
2556. 5 : 6-dinitrotetralin (dinitrotetrahydronaphthalene) yields chiefly 5-nitro-6-aminotetralin with some 6-nitro-5-aminotetralin.

2557. Similarly from the corresponding dinitrocompounds we get ortho-nitro-para-toluidine, 6-nitro-ortho-toluidine, and 1-nitro-2-methyl-8-naphthylamine.

2558. From a mixture of 1 : 5- and 1 : 8-dinitro-2-methylnaphthalenes we get only the 8-amino-derivative. [Vesely and Rein, *Archiv. Hemiju*, 1927, **7**, 55.]

2559. Dinitrobenzenes to Phenylenediamines (Diamido-benzols). Gas phase 190°-210° : nickel catalyst. At 250° there occurs a breaking up of the molecule, ammonia is given off and aniline formed. [Mignonac, *Bull. Soc. Chim.*, 1910 (4), **7**, 154.]

2560. Over copper at 320°-330° the reaction starts on the same path, but stops owing to formation of what seems to be a condensation product of the nitro- and amido-compounds.



[*Ibid.*]

2561. Nitranilines to phenylene diamines. Brown and Carrick²⁷ were, however, successful in making phenylene-diamines by hydrogenating nitranilines in the gas phase, over copper on pumice. The ortho- and para- compounds were treated at about 195°-250° C. the meta-compound at 255°-310° C. In each case the reaction was very slow.

2562. Dinitrotoluenes to cresyl-diamines. Gas phase : 175°-180°, nickel catalyst. Above 190° the molecule breaks up with evolution of ammonia and formation of aniline. [Mignonac, *Bull. Soc. Chim.*, 1910 (4), **7**, 823.]

2563. 2 : 4-Dinitrophenol to 3-nitro-2 aminophenol. Nickel catalyst : 8-10 atmospheres pressure. The hydrogenation continues with formation of 2 : 4 diaminophenol.

2564. 2 : 4 Dinitro 4' hydroxydiphenylamine gives the diamino compound. [Feldmann, *Giorn. Chim. Ind. Appl.*, 1925, **7**, 406.]

2565. *o*-Nitracetophenone to *o*-aminacetophenone. Aqueous alcohol solution, colloidal palladium catalyst : 1 atmosphere plus pressure. [Skita and Meyer, *Ber.*, 1912, **45**, 3579. Also with colloidal platinum. [*Ibid.*]^{27a}

2566. Ethyl 4 hydroxymethyl-3-nitrobenzoate to ethyl 4 hydroxymethyl 3 amino-benzoate.

2566A. (1) By Skita's method: Nitro ester 5 g., 40 cc. glacial acetic acid, 30 cc. water, 0.2 g. colloidal platinum (Skita) : 2-5 atmospheres pressure of hydrogen : two hours' shaking : 82 per cent yield.

2566B. (2) With Voorhees-Adams platinum oxide catalyst: 10 g. nitro ester, 70 cc. acetic acid, 40 cc. water, 0.33 g. catalyst, a few drops ferric chloride solution : three hours' shaking in hydrogen at 2-3 atmospheres pressure : 44 per cent yield.

2567. The *n*-butyl nitro ester was also hydrogenated to the amino compound in (50 per cent) alcohol acidified with hydrochloric acid in presence of colloidal platinum. [Case, *J. Am. Chem. Soc.*, 1925, **47**, 3007.]

2568. Cholesteryl para-nitrobenzoate to cholesteryl para-amino benzoate. Ethyl acetate solution : Adams platinum oxide catalyst. Reduction took only twenty-five minutes and the double bond of the cholesteryl radicle was unaffected.

With a large quantity of catalyst, cholesterol in ethyl acetate solution can be completely reduced to dihydrocholesterol in four hours.

2569. Dihydrocholesteryl para-nitrobenzoate was also hydrogenated to the para-aminobenzoate. [Shriner and Ko, *J. Biol. Chem.*, 1928, **80**, 1; *Chem. Abstr.*, 1929, **23**, 845.]

²⁷ *J. Am. Chem. Soc.*, 1919, **41**, 436.

^{27a} For reduction of some isonitroso ketones see para. 2696.

2570. γ -Substituted piperidinopropyl-*p*-nitrobenzoate hydrochlorides to the corresponding amino derivatives. [McElvain, *J. Am. Chem. Soc.*, 1927, **49**, 2835. Cf. Andrews and McElvain, *Ibid.*, 1929, **51**, 887.]

The interest of these products is due to the large number of local anesthetics belonging to the series.

2570A. See: Bolyard and McElvain, *J. Am. Chem. Soc.*, 1929, **51**, 922; *Chem. Abst.* 1929, **23**, 1902, for the reduction of 1-alkyl-4-piperidyl-*para*-nitrobenzoates to the corresponding *para*-aminobenzoates. The methyl, ethyl, propyl, butyl, isoamyl, and phenylethyl-compounds are described.

2570B. See: Marvel and Shelton, *J. Am. Chem. Soc.*, 1929, **51**, 915; *Chem. Abst.* 1929, **23**, 1902, for the similar preparation of the *para*-amino-benzoates derived from *N*-alkyl (methyl, ethyl and propyl) derivatives of 2- $[\beta$ -hydroxyethyl] piperidine.

2571. Cyclic Alkamine Esters of *Para*-aminobenzoic Acid. The following were made by catalytic reduction of the corresponding nitro-compounds in ethyl or butyl alcohol solution with hydrogen and the Adams platinum oxide-platinum-black catalyst:

- (1) *trans*-*o*-diethylaminocyclohexyl-*p*-aminobenzoate hydrochloride;
- (2) *m*-dimethylaminocyclohexyl-*p*-aminobenzoate hydrochloride;
- (3) *m*-diethylaminocyclohexyl-*p*-aminobenzoate hydrochloride;
- (4) (? *cis*-) *p*-dimethylaminocyclohexyl-*p*-amino-benzoate hydrochloride.
- (5) (? *trans*-) *p*-dimethylaminocyclohexyl-*p*-aminobenzoate hydrochloride.

All these are local anesthetics both on mucous surfaces and by injection, (5) is slightly more powerful, in this respect, than cocaine. [Heckel and Adams, *J. Am. Chem. Soc.*, 1927, **49**, 1303.]

2572. γ -Nitro ketones in solution or suspension in methanol shaken with hydrogen and platinum-black give reduced condensation products, the course of the reactions being difficult to follow and seeming capricious.

2572A. γ -Nitro- β -phenylpentanone gives 2-methyl-4-phenylpyrrolidine.

2572B. β -3, 4-Methylenedioxyphenyl- γ -nitrobutyrophenone gives the γ -amine compound. But, without other known change in the conditions, this reduction was interrupted at an earlier stage and the products obtained (with unaltered γ -nitro ketone) were 1-hydroxy-2-phenyl-4-[3, 4-methylenedioxy-phenyl] pyrroline and 2-phenyl-4-[3, 4-methylenedioxyphenyl] pyrrolidine. A nitro-ketone, $O_2NCH_2CHC_6H_4CH_2COC_6H_5$, gave oily products. [Kohler, *J. Am. Chem. Soc.*, 1923, **45**, 2144.]

2573. Nitrostilbene to diphenylethanone-oxime (oxime of desoxybenzoin). 4.6 g. nitrostilbene in 100 cc. ether : 0.1 g. platinum-black : shaken with hydrogen. [Kohler and Drake, *J. Am. Chem. Soc.*, 1923, **45**, 1286.]

2574. 2-Bromo-3-*p*-nitrobenzoyl-mesitylene to 2-bromo-4-*p*-amino-benzoylmesitylene. In ethanol solution : Adams platinum-black catalyst. In ethyl acetate solution an azo-derivative is formed as a by-product.

2574A. 2-Bromo-4-*mm'*-dinitro-benzoylmesitylene gives 2-bromo-4-*mm'*-diaminobenzoylmesitylene. [Hyde and Adams, *J. Am. Chem. Soc.*, 1928, **50**, 2499.]

2575. β , β -Diphenyl-nitro-ethylene to diphenyl-acetalimine. Solution in dry ether: Willstätter's platinum-black catalyst. [Kohler and Drake, *J. Am. Chem. Soc.*, 1923, **45**, 1286.]

2575A. β , β -Diphenyl-dinitro-ethylene treated in the same manner proved difficult to hydrogenate, successive additions of catalyst failing to carry the reduction to completion. Among the products were recognized: benzophenone, diphenylacetonitrile and tetraphenyl-succinonitrile. [*Ibid.*]

2576. Benzoyl-phenyl-nitrocyclopropane (methyl alcohol solution) yielded β -phenyl- γ -nitro-butyro-phenone. [*Ibid.*]

2577. α -Nitronaphthalene to α -naphthylamine. Gas phase : 300° : nickel catalyst. At higher temperatures, especially at 380°, ammonia, naphthalene and tetrahydronaphthalene are also formed. Copper may also be used as a catalyst at 330°-350°. [Sabatier and Senderens, *Compt. rend.*, 1902, **135**, 226.]

2578. α -Nitronaphthalene to α -naphthylamine. 5 g. in 100 cc. glycol : palladium

black 0.2 g. : 3.3 atmospheres hydrogen pressure : seven and one-half hours. Yield: 89.4 per cent in three hours; 98.4 per cent in three hours at 6½ atmospheres. Solvents in increasing order of efficiency were: glycerol, glycol, water, isopropyl alcohol. A high yield of the amine is given in one and one-half hours, with palladous and platinum oxide catalysts. The fused nitronaphthalene with palladium oxide yielded 93.9 per cent amine, with nickel, 14.3 per cent. [Parrett and Lowy, *J. Amer. Chem. Soc.*, 1926, **48**, 778; *Chem. Abst.*, 1926, **20**, 1232.]

2579. α -Naphthylamine.²⁸ α -Nitronaphthalene is catalytically reduced to α -naphthylamine by heating and agitation in an autoclave with water, hydrogen and a catalyst such as finely divided nickel, cobalt, copper or iron or one of their oxides and a carrier such as pumice, charcoal or quartz. The starting material should be free from organic halogen compounds, and from sulphur, tellurium and selenium.²⁹

2580. 1-Nitronaphthol (2) to aminonaphthol. Ether or acetone solution; platinum-black catalyst, 1 per cent of platinum by weight of substrate : reduction complete in few minutes. [Cusmano, *Lincei*, 1917, **26** (2), 87.]

2581. Sodium 1-nitroso- β -naphthol-6-sulphonate hydrogenated under a pressure of 8-10 atmospheres with a nickel catalyst gives the amino compound (eikonogen).

2582. 1 : 5-Dinitronaphthalene-3 : 7-disulphonic acid gives the diamino-acid. [Feldman, *Giorn. Chim. Ind. Appl.*, 1925, **7**, 406.]

2583. Preparation of Aminoanthraquinones.³⁰ α -Nitroanthraquinones are reduced with hydrogenated quinolines in presence of acetic acid, pyridine, *o*-dichloro-benzene, quinaldine, or other diluent. The final mixture of quinaldine and excess unoxidized tetrahydroquinaldine may be catalytically hydrogenated and used again. 1 : 5-Dinitroanthraquinone affords 1 : 5-diaminoanthraquinone or 5-nitro-1-aminoanthraquinone; 1 : 5-dichloro-4-aminoanthraquinone and 8-nitro-1-aminoanthraquinone are similarly obtained.³¹

²⁸ Poma and Pellegrini, *Brit. Pat.* 227,481, Aug. 27, 1923.

²⁹ *Chem. Abst.*, 1925, **19**, 2673.

³⁰ U. S. Pat. 1,691,428, Nov. 13, 1928, to Berthold, assignee to Grasselli Dyestuffs Corp.

³¹ *Brit. Chem. Abst.*, 1929, 237B.

CHAPTER XXVI

HYDROGENATIONS AT NITROGEN LINKAGES

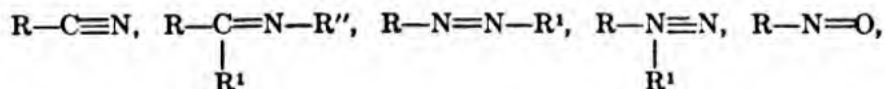
II

NITRILES, OXIMES, ETC.

2600. The Catalytic Reduction of Hydrogen Cyanide. When hydrogen cyanide vapor and hydrogen are passed over heated metallic catalysts, mono-, di-, and trimethylamine, ammonia and methane are formed. Barratt and Titley investigated the variation in the products caused by a variation in catalyst and conditions. Platinum catalysts were used, as preliminary experiments had shown that finely divided iron was not suitable. Asbestos fiber soaked in platinum chloride solution was dried and reduced in hydrogen at 150°. Preparations with less than 10 per cent platinum were found unutilizable and 20 per cent platinized fiber was most frequently employed; platinum percentage affected efficiency of the process and not the nature of the products. Liquefied hydrocyanic acid (previously dried with calcium chloride) was mixed with hydrogen and passed through 20–30 cm. of asbestos in a 1.3-cm. tube, the basic reduction products being absorbed by passage through aqueous hydrochloric acid. The reduction begins at 120°; the nature of the products, while independent of temperature between 120° and 250°, is dependent on the partial pressure of the hydrogen cyanide in the gas mixture, the primary amine increasing as hydrogen cyanide pressure is decreased, while the di- and trimethylamines yield is reduced. With low pressure of hydrogen cyanide a 70 per cent yield of methylamine and a 10 per cent yield of di- and trimethylamine were obtained. The continued use of the catalyst led to an increase in ammonia and decrease in amine production; the original activity of the catalyst was restored by treatment with chlorine. Dehydrogenation and auto-reduction of methylamine occurred above 300° C.¹

2601. Hydrocyanic Acid to Methylamine. Platinum-black catalyst. [Debus, *Annalen*, 1863, 128, 200.] This is the first recorded catalytic hydrogenation of an organic compound.

2602. Hydrogenating Open Chains Containing Nitrogen in Unsaturated Union. It has been found that open chains which contain nitrogen in unsaturated union such as



e.g., hydrocyanic acid, cyanic acid, isocyanic acid, salts or esters of these acids, nitriles, nitroso-compounds, imino-esters, aldehyde-imines, amidines, diazonium compounds, diazotates, can be hydrogenated in the presence of a catalyst such as nickel, if the operation is conducted in liquid phase in the presence of an electrolyte which yields at

¹ Barratt and Titley, *J. Chem. Soc.*, 1919, 115, 902. Cf. Catalytic hydrogenation (of nitriles) under pressure with nickel catalysts. Braun and others, *Ber.*, 1923, 56B, 1988; *Chem. Abst.*, 1924, 18, 675.

least as many acid ions as correspond with the base produced.¹ The operation is carried out in aqueous solution. Potassium cyanide is reduced to methylamine by hydrogen and nickel in presence of ferrous sulphate. Acetonitrile gives ethylamine, phenylacetone, β -phenylethylamine; azobenzene, cyclohexanol and cyclohexylamine.²

2603. Ethyl cyanide to dipropylamine (75 per cent). Gas phase : 200° : nickel catalyst. [Sabatier and Senderens, *Compt. rend.*, 1905, **140**, 482.] In addition to dipropylamine there were formed 8 per cent of propylamine and 16 per cent of tripropylamine.

2604. In aqueous alcohol, with a nickel catalyst, ethyl cyanide (propionitrile) showed little evidence of hydrogenation, only 26 per cent of the amount of hydrogen for 1 molecule being absorbed; the nitrile was for the most part unchanged.

2605. Butyl cyanide (*n*-valeronitrile) gave diamylamine. [Rupe, Metzger and Vogler, *Helv. Chim. Acta*, 1925, **8**, 848; *Chem. Abst.*, 1926, 1216.]

2605A. Ethylene dicyanide to tetramethylene-diamine. Gas phase : 180°–200° :

over nickel. Ammonia and pyrrolidine $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{array} \text{NH}$ are also formed. [Gaudion, *Bull. Soc. Chim.*, 1910 (4), **7**, 824.]

2606. β -Methylbutyronitrile to diisoamylamine (and ammonia). [Rupe and Hodel, *Helv. Chim. Acta*, 1924, **7**, 1023.]

2607. Isoamyl cyanide over nickel at 200° gives the secondary amine in good yield. The primary and tertiary amines as well as a little isopentane are also formed. [Sabatier and Senderens, *Compt. rend.*, 1905, **140**, 482.]

2608. Hydrogenation of Cyano Compounds. Cyanoacetylurea, hydrogenated at 60°–70° in 60 parts of water, with 2 parts of nickel catalyst, yielded uracil. Rupe, Metzger and Vogler, *Helv. Chim. Acta*, 1925, **8**, 848; *Chem. Abst.*, 1926, **20**, 1216.

2609. Preparation of Primary Amines by the Catalytic Reduction of Nitriles. *p*-Toluenitrile is reduced smoothly in acetic anhydride solution by hydrogen in presence of platinum oxide, with formation of *p*-methylbenzylacetamide, in 88 per cent yield. The reduction requires over five hours with hydrogen under 3 atmospheres pressure. In glacial acetic acid, a 71 per cent yield of *pp'*-dimethyldibenzylamine, together with small proportions of the corresponding primary and tertiary amines, was obtained similarly in six and one-half hours. In absolute alcohol, reduction proceeds more slowly, and both primary and secondary amines are produced. In *n*-butyric anhydride, a 74 per cent yield of *p*-methylbenzyl-*n*-butyramide, m.p. 71°–72°, was obtained. Benzonitrile affords similarly, in acetic anhydride solution, benzylacetamide; in glacial acetic acid, benzylamine and dibenzylamine, the former predominating; and in absolute alcohol, ammonia and the primary and secondary amines. *o*-Toluenitrile is reduced similarly in acetic anhydride solution to *o*-methylbenzylacetamide, while phenylacetone affords β -phenylethylacetamide, in 63 per cent yield. The success of the preparation of primary amines by reduction of nitriles in acid anhydride solution is ascribed to prevention of hydrolysis of the imine usually assumed to be formed immediately, and to prevention of its condensation with the primary amine by the prior acylation of the latter.⁴

2610. Benzonitrile to benzylamine and dibenzylamine. Gas phase : 250° : nickel catalyst : reaction incomplete : residual nitrile removed by a current of steam after neutralization of the amines with hydrochloric acid. [Frébault, *Compt. rend.*, 1905, **140**, 1036.]

¹ Brit. Pat. 304,000, Dec. 20, 1927, to Imray, from I. G. Farbenind. A.-G.; *Chem. Age* (London), 1929, **20**, 188.

² Brit. Chem. Abst., 1929, 235B.

⁴ Brit. Chem. Abst., 1926, 161A. Carothers and Jones, *J. Am. Chem. Soc.*, 1925, **47**, 3051. Cf., Fr. pat. 647,090, May 23, 1927 to Mignonnac; *Chem. Abst.*, 1929, **23**, 2446.

2610A. According to Komatsu and Ishida,⁵ the reduction of benzonitrile by hydrogen in presence of reduced copper at 150°–200° gives a mixture of benzaldehyde, benzylamine, and dibenzylamine. The yield of bases is favored by a low temperature (150°) and by those forms of reduced copper that are most active as oxidizing catalysts. A rapid current favors the formation of aldimine. At a higher temperature the nitrile is decomposed to toluene and ammonia. The reduction of acetonitrile and isovaleronitrile gives no aldimine but only primary and secondary amines.⁶

2610B. *o*-Phenylbenzonitrile to *o*-phenylbenzylamine. Nickel catalyst; 15–20 atm.; 120°–130° C. [v. Braun and Manz, *Ann.*, 1929, **468**, 258].

2611. On hydrogenation with colloidal palladium in aqueous alcohol benzonitrile yielded benzylamine, dibenzylamine, ammonia and a small quantity of benzaldehyde. [Paal and Gerum, *Ber.*, 1909, **42**, 1553.]

2611A. Benzaldoxime gave the same products.⁷

2612. Mandelonitrile gave benzylamine, dibenzylamine, ammonia and benzyl alcohol.⁸ [Paal and Gerum, *loc. cit.*]

2613. *p*-Toluenitrile, hydrogenated in the gas phase at 250° over nickel, gives a mixture of the primary and secondary amines, i.e., para methylbenzylamines. [Frébaud, *Compt. rend.*, 1905, **140**, 1036.]

2614. Phenylacetonitrile hydrogenated, under reduced pressure, in presence of platinum oxide or reduced nickel yields α -phenyl- β -imino-ethane (β -phenylacetaldimine).

2614A. Benzonitrile hydrogenated at low pressure in presence of nickel gives (unstable) benzaldehyde. [Grignard and Escourrou, *Compt. rend.*, 1925, **180**, 1883.] For apparatus and method see: Escourrou, *Thèse d'Etat*, Lyon, 1925.

2614B. The catalytic hydrogenation of nitriles in glacial acetic acid with a palladium catalyst leads to the production of primary amines, whereas Paal and Gerum [*Ber.*, 1909, **42**, 1553] and Rupe and Glenz working in aqueous alcohol or in a neutral solvent obtained mainly secondary amines.

2614C. Phenylacetonitrile gave β -phenylethylamine.

2614D. *o*-Chlorobenzonitrile gave *o*-chlorobenzylamine, in the presence of concentrated sulphuric acid and benzylamine in the presence of sodium acetate.

2614E. *p*-Hydroxyphenylacetonitrile, on the other hand, formed di- β -*p*-hydroxyphenylethylamine, this can be inhibited, partly, by the addition of quinoline, with the production of some β -*p*-hydroxyphenylethylamine. Helianthin yields *p*-aminodimethylaniline. [Rosenmund and Pfankuch, *Ber.*, 1923, **56**, 2258.]

2614F. *p*-Tolylacetonitrile. β -*p*-tolylethylamine. [Braun and Wirz, *Ber.*, 1927, **60B**, 102.]

2615. In alcohol-water solution acetophenylacetonitrile gave methylbenzyl ketone (volatile with steam) and α -acetophenylacetaldehyde aldimine. [Rupe, Metzger and Vogler, *Helv. Chim. Acta*, 1925, **8**, 848; *Chem. Abst.*, 1926, **2D**, 1216.]

2616. Hydroxymethylenephénylacetonitrile, $C_6H_5(CN):CH:OH$ to hydroxymethylene phenylacetaldimine. Nickel catalyst: atmospheric pressure: room temperature. This aldimine, on hydrolysis, yields the aldehyde. [Rupe and Knap, *Helv. Chim. Acta*, 1927, **10**, 299.]

2617. The hydrogenation of diphenylacetonitrile with a nickel catalyst stops when some 75 per cent of the amount of hydrogen calculated for 2 molecules is absorbed. The products are α , α -diphenylethylamine (30 per cent), a small quantity of *sec*-di [α , α -diphenyl] amine, and some benzophenone. [Rupe and Gisiger, *Helv. Chim. Acta*, 1925, **8**, 338; *Chem. Abst.*, 1925, **19**, 2822.]

2618. Triphenylacetonitrile is reduced slowly to triphenylethylamine. [*Ibid.*]

2619. Cyanomethylantronic acid, $m\text{-NCCH}_2\text{NHC}_6\text{H}_4\text{COOH}$, reduces to a mixture of unascertained composition. [*Ibid.*]

⁵ *Mem. Coll. Sci.*, Kyoto, 1927, 331.

⁶ *Brit. Chem. Abst.*, 1928, 286A.

⁷ See para. 2634.

⁸ See paras. 2635, 2636.

2620. Hydrocyanodiphenylcarbodiimine, $C_6H_5NHC(CN):NC_6H_5$ is hydrogenated also in a complicated way, the only products isolated were aniline and hydrocyanic acid. [*Ibid.*]

2621. α -Phenyl- β -benzoyl-propionitrile gives a primary base which immediately parts with water producing diphenylpyrroline, and a small quantity of an isomeric base. Reduction of the same nitrile in boiling alcohol-ethylacetate mixture gives diphenylpyrroline and diphenylpyrrolidine. [*Ibid.*]

2622. α -Cyanodesoxybenzoïn gives the aldimine of benzoylphenylacetaldehyde, which changes to the enol form, hydroxymethyl desoxybenzoïn. [*Ibid.*]

2623. α , β -diphenyl- β -phenacylpropionic nitrile (2 isomers) to triphenylpiperidine. In ethyl acetate-alcohol-water solution: nickel catalyst. [Rupe and Stern, *Helv. Chim. Acta*, 1927, 10, 859; *Chem. Abst.*, 1928, 22, 779.]

2624. Hydroxymethylenephénylacetaldehyde (aldime) is produced in 80 per cent yield by catalytic reduction of hydroxymethylenephénylacetonitrile in aqueous alcohol solution with a nickel catalyst. See para. 2616.

2625. α - γ -Ethoxypropylbenzonitrile in decalin at 30 atmospheres and 100°, with a nickel catalyst, is hydrogenated to a mixture of α - γ -ethoxypropylbenzylamine and (apparently) ϕ Li di- α - γ -ethoxy-propylbenzylamine. [von Braun and Kaiser, *Ber.*, 1925, 58, 2162.]

2626. Ethylbenzene Series, Basic Derivatives. *p*-Nitrophenylacetonitrile p - $O_2NC_6H_4CH_2CN$ to *p*-aminophenylacetonitrile p - $H_2NC_6H_4CH_2CN$. Tetralin solution (10 per cent): 120°: Nickel catalyst. If at this stage the temperature is raised to 130° there are formed β -*p*-aminophenylethylamine p - $H_2N \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NH_2$ and *bis*-[β -*p*-aminophenylethyl] amine, $(H_2N \cdot C_6H_4 \cdot CH_2 \cdot CH_2)_2NH$. *p*-Hydroxyphenylacetonitrile p - $HOC_6H_4CH_2CN$ in tetralin at 120°-130° with nickel catalyst gives tyramine and *bis* [β -*p*-hydroxyphenylethyl] amine. In cyclohexanol it is readily reduced at 120°-130° to *N*-cyclohexyl- β -*p*-hydroxyphenylethylamine (55 per cent), *bis* [β -*p*-hydroxyphenylethyl] amine (18 per cent), tyramine (8 per cent). *p*-Aminophenylacetonitrile p - $H_2NC_6H_4CH_2CN$, in cyclohexanol at 90° with nickel catalyst, gives 40-45 per cent of [β -*p*-aminophenylethyl] cyclohexylamine. [von Braun and Blessing, *Ber.*, 1923, 56B, 2153; *Chem. Abst.*, 1924, 822.]

2627. 1,5-Cyano-nitronaphthalene (nitronaphthalene nitrile), in ethyl acetate-alcohol-water solution, with nickel catalyst, was hydrogenated to 1,5-aminonaphthalene-nitrile. 2,5-cyano-nitronaphthalene and 1, 2-cyano-nitronaphthalene behaved in the same manner. [Rupe and Metzger, *Helv. Chim. Acta*, 1925, 8, 838; *Chem. Abst.*, 1926, 20, 1216.]

2627A. 1,4-Cyano-naphthalene-sulphonate of sodium in aqueous solution, with nickel catalyst, gave on acidification 4-sulphonaphthomethylamine. [*Ibid.*]

2627B. 1,5-Cyano-bromo-naphthalene gave 1,5-bromo-naphthaldehyde (12 per cent) di[5,1-bromo naphthylmethyl] amine (7 per cent) and 5-bromo-1-naphthylmethylamine. [*Ibid.*]

2627C. 2,5-Cyano-bromo-naphthalene gave 5-bromo-2-naphthaldehyde (15 per cent), 5-bromo-2-naphthylmethylamine (62.5 per cent) and 2.5 per cent of what was probably the secondary amine. [*Ibid.*]

2627D. Salicylo-nitrile gave a green product containing nickel. This, purified by oxalic acid, yielded di[*o*-hydroxybenzyl] amine. [*Ibid.*]

2628. Cyanoketo Derivatives. Ethyl benzylidene cyanoacetate and ethyl benzylcyanoacetate both yield aldehyde of ethyl benzyl malonate.

Ethyl- α -nitrobenzylidene cyanoacetate to ethyl 2-amino-quinoline-3-carboxylate.

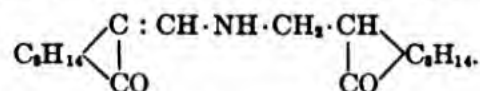
Ethyl- β -phenyl- γ -benzyl- α cyanobutyrate to ethyl-1:3-diphenylpiperidine-4-carboxylate. [Rupe and Heckendorn, *Helv. Chim. Acta*, 1926, 9, 980.]

2628A. Rupe and Pieper describe the hydrogenation, in aqueous alcoholic solution with a nickel catalyst, of ethyl phenylcyanopyruvate, of ethyl benzoylcianoacetate, and of ethyl benzylidenecyanoacetate. [*Helv. Chim. Acta*, 1929, 12, 637; *Brit. Chem. Abst.*, 1929, 938A.]

2629. Cyanidin chloride to *dl*-epicatechin. Methanol hydrogen chloride solution at 0°: platinum catalyst.

2630. Cyanidin chloride pentamethyl ether to racemic mixture of pentamethyl ethers of epicatechin. Alcohol solution: platinum catalyst. [Freudenberg, Fikentscher, Harder and Schmidt, *Ann.*, 1925, **444**, 135.]

2631. α -Cyano camphor to α -camphomethylamino-methylene camphor:



[Rupe and Hodel, *Helv. Chim. Acta*, 1924, **7**, 1023.]

2631A. Rupe describes the production of hydrocyclic ω -amino compounds by the hydrogenation of cyanocamphor, or other hydrocyclic cyanoketones, in presence of a nickel catalyst.⁹

2632. Aliphatic Oximes: Hydrogenation with Nickel at Low Temperatures.¹⁰ *Preparation of Catalyst.* Nickel carbonate was precipitated by sodium carbonate from the nitrate on kieselguhr. The kieselguhr had been freed from iron by treatment with concentrated nitric acid, followed by thorough washing with water. The impregnated and sifted guhr was reduced in hydrogen at 280°–330° C. (Thirty hours at least for every 10 g. of catalyst.)

2632A. Procedure. Acetaldoxime (2.1 g.) in 40 cc. water, under 1 atmosphere excess pressure at room temperature, absorbed 56 per cent of the calculated quantity of hydrogen in twenty-seven minutes. When CO₂ was passed into the tube containing the reduced catalyst and into the reaction flask, 85 per cent of the hydrogen was taken up in four hours. With absolute alcohol instead of water as solvent 93 per cent was absorbed in three hours. *Product:* Diethylamine, with ammonia. Propionaldoxime gave propylamine and ammonia. Isobutyraldoxime gave isoamylamine and ammonia.

2633. Hartung finds that, though previous investigators report that the catalytic reduction of oximes and nitriles results in a mixture of primary amine, secondary amine and ammonia, if benzaldoxime or benzonitrile is reduced by means of palladinized charcoal in absolute alcoholic solution containing hydrogen chloride, good yields of pure benzyl amine are obtained. Mandelonitrile reduced under similar conditions forms phenylethylamine in about 50 per cent yields. The benzoate and acetate of mandelonitrile are also reduced to phenylethylamine and in better yields.¹¹

The catalyst was palladinized charcoal: 3 g. pure animal charcoal shaken, in 1 atmosphere of hydrogen, with 0.45 to 0.5 g. palladium chloride: washed and dried.

2634. Benzaldoxime to Benzylamine. Absolute alcohol (40 cc.), oxime 3 g., with 3 equivalents of hydrochloric acid: ninety minutes: almost quantitative yield. With less hydrochloric acid some secondary amine forms.

2635. Benzonitrile to Benzylamine, in the same conditions, but one equivalent of HCl sufficed to prevent formation of the secondary amine.

2636. Mandelonitrile to Phenylethylamine 5.8 g. (0.0436 mole) nitrile in 90 cc. absolute alcohol with 0.049 HCl. The expected phenylethanolamine was not obtained, but a 52 per cent yield of phenylethylamine with a large amount of a non-basic by-product resulted.¹²

2637. Mandelonitrile Benzoate to Phenylethylamine. 5.9 g. (0.025 mole) benzoate in 60 cc. absolute alcohol with 0.057 mole HCl: 84.5 per cent yield. Using only one equivalent of HCl leads to poor yields and secondary reactions. Mandelonitrile acetate gave phenylethyl amine in 74.5 per cent yield.

⁹ U. S. Pat. 1,670,990, May 22, 1928. Cf. Brit. Pat. 240,814, Oct. 1, 1928, to Rupe; *Chem. Abst.*, 1926, **20**, 2167.

¹⁰ Vassiliev, *Ber.*, 1927, **60B**, 1122; *Chem. Abst.*, 1927, **21**, 2457.

¹¹ Hartung, *J. Am. Chem. Soc.*, 1928, **50**, 3370.

¹² See paras. 2610–2612.

2638. Catalytic Reduction of Oximes and Nitriles and a Method for the Preparation of Secondary Amines. [K. W. Rosenmund and G. Jordan, *Ber.*, 1925, **58B**, 51-53.] Benzylamine is converted into dibenzylamine and ammonia to an extent greater than 90 per cent when heated in boiling xylene in a current of hydrogen in the presence of palladized barium sulphate; if the hydrogen is replaced by air large quantities of benzylidenebenzylamine are produced, while in the presence of nitrogen the products are dibenzylamine and benzylidene-benzylamine (10-15 per cent). β -Phenylethylamine gives di- β -phenylethylamine in 88 per cent yield. Benzene, toluene, and cumene are less suitable than xylene as solvents.¹³

2639. Catalytic Action of Reduced Copper on Oximes. Oximes are classed into three groups according to the nature of the products formed by the contact action of reduced copper at 200° in an atmosphere of hydrogen. Group 1 contains those (e.g., benzophenoneoxime) that yield mainly aldehydes or ketones (which are transformed into hydrocarbons) and some basic compounds; group 2 comprises benzaldoxime and benzhydroxamic acid, an acid amide being produced which changes into a nitrile and an acid, while members of group 3 (e.g., acetophenoneoxime) show an intermediate behavior. The various products are considered to be formed by the varying catalytic action of copper on the successive thermal reactions: (a) Beckmann's transformation, (b) conversion into ketone or aldehyde, (c) conversion into imine or nitrile. The catalytic action is explained by the formation of an intermediate compound between the copper and the oxime, together with the supposition of a hydride CuH_2 . When the copper loses electrons so that the combining force between the hydrocarbon radicals and the carbon atom of the methane nucleus of the oxime is smaller than that between the nitrogen and the carbon atoms, the Beckmann transformation occurs (group 2). When the opposite holds, and the metal exerts no appreciable influence on the combining forces, an aldehyde or ketone is formed (Group 1). [Yamaguchi, *Bull. Chem. Soc., Japan*, 1, 54; *Brit. Chem. Abst.*, 1926, 50, 616, 952A.]

2640. Oximes and nitriles to primary amines. Vapor phase or liquid phase: nickel or copper. Catalyst: hydrogen and ammonia.

2640A. Examples: Acetonitrile to ethylamine at 180° C. (Vapor.)

2640B. Benzonitrile to benzylamine, at 250° C. copper catalyst. (Vapor.)

2640C. Propanone oxime to 2-aminopropane. (Vapor.)

2640D. Acetonitrile to ethylamine. (Solution in alcoholic ammonia with ammonium chloride.)

2640E. Benzyl cyanide to β -phenylethylamine.

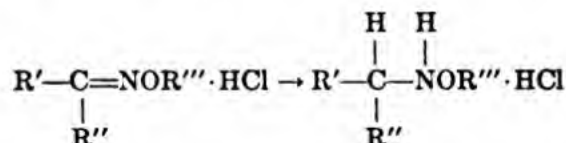
2640F. Benzonitrile, nickel catalyst at 100° C. (Liquid phase.¹⁴)

2641. Variation in Hydrogenation of Oximes. Ethyl β -aminobutyrate is not formed by the catalytic hydrogenation of ethyl β -oximinobutyrate in aqueous-alcoholic solution in the presence of colloidal palladium; the observed absorption of hydrogen is due to fission of the oxime and reduction of the liberated hydroxylamine to ammonia. Acetoxime and methyl ethyl ketoxime could not be reduced under similar conditions, although the potential activity of the catalyst remained unaltered. Benzaldoxime, on the other hand, yields a mixture of mono- and di-benzylamine, ammonia, and benzaldehyde. Benzophenoneoxime gives diphenylmethylamine, but acetophenone-oxime and dibenzylketoxime could not be reduced. Acetaldoxime and propaldoxime are reduced exclusively to the corresponding tertiary amines. Reduction takes place only at the commencement of the experiment; subsequently, when the reaction appears to proceed more slowly, the oxime probably becomes hydrolyzed and the liberated hydroxylamine is converted into ammonia. The production of the tertiary amine is not due to elimination of ammonia from preformed, primary amine. [Gulevich, *Ber.*, 1924, **57B**, 1645, *J. Chem. Soc.*, 1924 (i), 1285.] The hydrochlorides of O-methylacetoxime, O-ethyl-

¹³ *J. Chem. Soc. Abst.*, 1925, i, 245.

¹⁴ *Brit. Pat.* application 282,083, convention date, Dec. 9, 1926, by Mignonac, assigned to Fabr. Prod. chim. org. de Laire; *Chem. Age*, 1928, **18**, 150; *French Pat.* 638,550, Dec. 9, 1926.

acetoxime and O-methyldiethyl-ketoxime have been catalytically reduced to the corresponding O, N-dialkyl hydroxylamine, according to the reaction:



There is some tendency to splitting with formation of ammonium chloride. [Jones and Major].

2642. Benzaldoxime acetate, benzophenoneoxime acetate, gallaldoxime acetate, on catalytic hydrogenation with palladium catalyst, yield, either solely or as chief product, the primary amine. Catalytic reduction of the oximes themselves produces, chiefly, the secondary amines. [Rosenmund and Pfankuch, *Ber.*, 1923, **56**, 2258.]

2643. Acetaldoxime to diethylamine: Gas phase: 150°-200°: nickel catalyst. [Sabatier: *Catalysis*, **383**.]

2644. Acetonoxime to one-third isopropylamine, with twice as much of di-isopropylamine and some tri-isopropylamine. Gas phase: 180°-220°: nickel catalyst. Mailhe, *Compt. rend.*, 1905, **141**, 113.]

2645. Primary amines are produced by hydrogenation of oximes in a solution of acetic anhydride. Thus, benzaldoxime gives acetyl benzylamine: acetophenone oxime gives the acetyl derivative of α -phenylethylamine. The free amines are obtained by hydrolysis. Nickel, cobalt, copper, etc., can be used as catalysts. [Mignonac, *Fr. Pat.*, 647,090, May 23, 1927: *Chem. Abst.* **1929**, 2446.]

2646. Dipropyl-ketoxime to δ -hydroxylaminoheptane. 70 per cent aqueous alcohol solution with hydrochloric acid: platinum-black catalyst.

2647. Methyl-isobutyl-ketoxime to β -hydroxyl-amino- δ -methylpentane.

2648. Acetophenone-oxime to β -hydroxylamino- β -phenylethane.

2649. Aldoximes similarly treated yield secondary hydroxylamines. *Examples:* heptaldoxime to diheptylhydroxylamine: isovaleraldoxime to di- γ -methylbutyl-hydroxylamine: benzaldoxime to dibenzyl-hydroxylamine: piperonaloxime to di-piperonyl-hydroxylamine. [Vavon and Krajcinovic, *Bull. Soc. Chim.*, 1928 (iv), **43**, 231.]

2650. Heptaldoxime, oenanthaldoxime $\text{C}_6\text{H}_{11}\cdot\text{CH}:\text{N}\cdot\text{OH}$ in the gas phase over nickel at 210°-220° is hydrogenated to the amines, the primary amine being the chief product (65 per cent). [Mailhe, *Compt. rend.*, 1905, **140**, 1691.]

2651. Cyclopentanone-oxime, in the gas phase, with a rapid current of hydrogen, over nickel, at 180°, gives a mixture of the three cyclo-pentyl-amines, the secondary amine predominating. [Sabatier and Mailhe, *Compt. rend.*, 1914, **158**, 985.]

2652. Dimethylglyoxime to the mono- and hemi-hydrates of $\beta\gamma$ -diaminobutane. Platinum-black: glacial acetic acid solution. [Frejka and Zahlova, *Publ. Fac. Sci. Masaryk*, 1926, **73**, 3. See also, *idem*, *J. Czechoslov. Chem. Comm.*, 1929, **1**, 173; *Brit. Chem. Abst.*, **1929**, 544A.]

2653. Oximes (all in vapor phase at 200° C. over reduced copper):

2653A. Furfuraldoxime to pyromucic acid amide, furfural, an acid and a base.

2653B. Benzamidoxime to benzylamine, benzyl alcohol, benzonitrile.

2653C. Cinnamylaldoxime to unidentified products.

2653D. Dibenzylketoxime to phenylacetamide, phenylacetic acid, dibenzylketone, phenylacetoneitrile.

2653E. Benzophenonoxime to various incompletely identified products.

2653F. Acetoxime to acetone, isopropylamine. [Yamaguchi, *Bull. Chem. Soc., Japan*, 1926, **1**, 35; *Ibid.*, 1927, **54**; *Chem. Abst.*, **21**, 75.]

2654. Furfural oxime in ether solution, with palladium-charcoal catalyst, was hydrogenated to di- α -furfuralamine. [Williams, *Ber.*, 1927, **60B**, 2509.]

2655. Vassiljev (Wassiljew). Catalytic reduction of aliphatic oximes with nickel at room temperatures. *Ber.*, May 11, 1927, 1122.

2656. Acetophenoxime, $C_6H_5 \cdot C(: NOH) \cdot CH_3$, gives mostly the secondary amine, di- α -phenylethylamine with some primary amine, $C_6H_5 \cdot CH(NH_2) \cdot CH_3$, and acetophenone regenerated by the reaction of the water produced on the oxime. Gas phase: 250° – 270° : nickel catalyst. [Mailhe and Murat, *Bull. Soc. Chim.*, 1911 (4), 9, 464.]

2657. Propiophenoxime. The vapors of propiophenoxime carried over nickel at 250° – 270° by a brisk current of hydrogen give a small amount of the primary and secondary amines with much phenyl-propylene and phenyl-propane. The hydrogenation is, therefore, unsatisfactory. [Mailhe and Murat, *Bull. Soc. Chim.*, 1911 (4), 9, 214.]

2658. Camphoroxime to dibornylamine. Gas phase: 180° – 200° nickel catalyst [Aloy and Brustier, *Bull. Soc. Chim.*, 1911 (4), 9, 734.] Some bornylamine, camphylamine and ammonia are also formed.

2659. Menthone-oxime over nickel at about 280° yields the primary and secondary menthyl-amines and some menthone. [Mailhe and Murat, *Bull. Soc. Chim.*, 1911 (4), 9, 464.]

2660. α -Terpineolbenzeneazohydroxylamineoxime to $C_{15}H_{25}N_4O_3$, probably an azo derivative. [D'Ambrosio, *Gazz. chim. ital.*, 1927, 57, 726; *Chem. Abst.*, 1928, 22, 775.]

2661. 2-Quinolylacetaldoxime to 2-quinolyl- β -ethylamine. Platinum catalyst. [Hupe and Schramme, *Z. physiol. Chem.*, 1928, 177, 315.]

2662. Amines from Aldehydes and Ketones. The vapor of the aldehyde or ketone (or their ammonia compounds), mixed with hydrogen and ammonia, is passed over a heated nickel catalyst: primary amines are produced. Cyclohexanone gives cyclohexylamine; *n*-butylaldehyde, *n*-butylamine; isobutylaldehyde, isobutylamine; propylaldehyde, propylamine; isovaleraldehyde, isoamylamine; isocaproic-aldehyde, isohexylamine. The catalyst is prepared by depositing basic nickel carbonate and water glass on pumice and reducing with hydrogen. An activating (dehydration) catalyst such as aluminum phosphate or alumina may also be present.¹⁵

2663. Secondary Bases of the Naphthalene Series [*dinaphthomethylamines*]. When α and β -naphthonitriles are reduced with hydrogen in the presence of nickel they yield respectively $\alpha\alpha$ - and $\beta\beta$ -dinaphthomethylamine, which are of use in the production of dyestuffs and drugs.¹⁶

2664. Hydroxybenzylamides of Unsaturated Fatty Acids [*pepper substitutes*]. The oximes of hydroxyaldehydes are reduced to salts of hydroxybenzylamines by treatment in acid alcoholic solution with hydrogen in the presence of palladium as catalyst, the palladium being either deposited on a carrier or precipitated, and the products are treated with unsaturated acid chlorides in the presence of aqueous sodium carbonate solution. For example, a solution of vanillyloxime in alcohol acidified with fuming hydrochloric acid is treated with hydrogen in the presence of palladium, and vanillylamine is obtained from the solution by filtration and evaporation *in vacuo*. Nonylenic acid chloride, undecylenic acid chloride, or oleic acid chloride is added gradually to a well-stirred solution of the product in lukewarm water, the solution having been made alkaline by the addition of sodium carbonate. The corresponding vanillylamide separates as an oil, and is purified by solution in alcohol and subsequent evaporation of the solvent. The products are suitable for use as substitutes for pepper.¹⁷

2665. Acetamide to ethylamine (and water). Gas phase: 230° : nickel or copper catalyst. Some ammonia is produced as well as dimethylamine, due to the decomposition of the ethylamine by the nickel. [Mailhe, *Bull. Soc. Chim.*, 1906 (3), 35, 614.]

2666. Propionamide to propylamine (and water). Gas phase: 200° : nickel or copper catalyst. [Mailhe, *Bull. Soc. Chim.*, 1906 (3), 35, 614.]

¹⁵ *Chem. Age*, 1927, 16, 402; Brit. Pat. application 265,960, Feb. 9, 1926, by I. G. Farben-ind. A.-G.

¹⁶ Swiss Pats. 108,704 and 109,066, June 30, 1923, to Rupe.

¹⁷ Ger. Pat. 383,539, Aug. 6, 1920, to Ott.

2667. Hexamethylene-tetramine, in the gas phase at 300°–350°, over nickel, yields ammonia, trimethylamine and methane. [Grassi, *Gaz. Chim. Ital.*, 1906, **36**, (2), 505.]

2668. 2, 2'-Azobispropane to symmetrical di-isopropylhydrazine. Colloidal platinum catalyst. [Lochte, with Noyes and Bailey, *J. Am. Chem. Soc.*, 1922, **44**, 2556.]

2669. Acetone-isopropyl-hydrazone also yields symmetrical di-isopropyl-hydrazine; when hydrogenated in this way. [*Ibid.*]

2670. Primary iso-propyl-hydrazine may be prepared by hydrogenating an equimolecular mixture of hydrazine hydrate, acetone and hydrochloric acid diluted (for 1 mol. of hydrazine hydrate) to 300 cc., in presence of colloidal platinum with gum arabic protective. [*Ibid.*]

2671. The mono-nitroso-derivative of the di-isopropyl-hydrazine broke up, on hydrogenation, into ammonia, symmetrical hydrazine and unidentified products. [*Ibid.*]

2672. Isobutaldazine with platinum-black catalyst is hydrogenated in stages. One molecule of hydrogen first combines in the $\alpha : \beta(\gamma : \delta) - \alpha : \delta$ -positions with formation of isobutylisobutyl-idenhydrazine, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$, and azoisobutane, $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{N} : \text{N} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$. A second molecule is taken up by these compounds produces *symm.* di-isobutylhydrazine (hydrazoisobutane), $\text{CH}(\text{CH}_3)_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3)_2$. This hydrogenates further to isobutylamine and di-isobutylamine. [Taipale, *J. Russ. Phys. Chem. Soc.*, 1925, **56**, 81.]

2673. Reduction of Azo Compounds to Hydrazo Compounds. Aromatic azo- and azoxy-compounds are reduced in good yield to the corresponding hydrazo-compounds by treatment in an organic solvent with hydrogen under pressure in presence of a nickel catalyst. By treating azobenzene in alcoholic solution at 100° with hydrogen under a pressure of 16.7 atmospheres in presence of reduced nickel, hydrazobenzene is obtained in satisfactory yield. At 126° and 33.3 atmospheres aniline is formed in quantitative yield. [Brown and Henke (assignors to Newport Co.), U. S. Pat. 1,589,936, June 22, 1926. *Brit. Chem. Abst.*, 1926, 816B.]

2674. Azobenzene, $\text{C}_6\text{H}_5 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_5$ to aniline. Gas phase : 290° : nickel catalyst. [Sabatier and Senderens, *Bull. Soc. Chim.*, 1906 (3), **35**, 259.] Also are formed small quantities of cyclohexylamine, dicyclohexylamine and ammonia. With colloidal palladium, under 2 atmospheres, azobenzene gives in five minutes hydrazobenzene, and this is hydrogenated more slowly (four and one-half hours) to aniline. [Skita, *Ber.*, 1912, **45**, 3312.]

2675. Acetone semicarbazone to isopropylsemicarbazide. 10 per cent chlorplatinic acid, 45 cc., gum arabic 0.5 g. in 10 cc. water, a small amount of germ colloid : reduce with hydrogen under 3 atmospheres pressure : add acetone semicarbazone, 15 g., hydrochloric acid (sp. gr. 1.2), 6.7 cc. : eight hours : 70 per cent yield. [Neighbors *et al.*, *J. Am. Chem. Soc.*, 1922, **44**, 1559.]

2676. Acetaldehyde phenylhydrazone, dissolved in ethyl alcohol, with similar treatment, yields the hydrazo compound. The same is true of acetone phenyl hydrazone. [*Ibid.*]

2677. Menthone semicarbazone to menthyl semicarbazide ($\text{C}_{10}\text{H}_{19}\text{NHNHCONH}_2$). Methyl alcohol solution : colloidal platinum catalyst as above : 4 atmospheres pressure : six to nine hours.

2678. Camphor semicarbazone hydrogenated in this way yields bornyl semicarbazide. [*Ibid.*]

2679. Di-isobutylideneazine (aldazine of isobutylaldehyde) was hydrogenated in the presence of platinum-black by method used previously for ketazine of acetone. [*J. Russ. Phys. Chem. Soc.*, 1923, **54**, 654, *Chem. Abst.*, 1923, **17**, 3015]. The best solvent was methanol. The hydrogenation takes place in two phases : First, 1 molecule of hydrogen absorbed produces the 2 isomers : isobutylisobutylidene hydrazine



and azoisobutane; secondly, another molecule of hydrogen unites with these compounds

forming *N,N*-di-isobutylhydrazine or hydrazo-isobutane (C_4H_9NH)₂. [Taipale, *J. Russ. Phys. Chem. Soc.*, 1925, **56**, 81, *Chem. Abst.*, 1925, **19**, 3478.]

2680. The influence of various factors on the speed of the catalytic hydrogenation of azines has been examined by Taipale.¹⁸ The catalyst used was platinum-black. For details of preparation and experimental technique the abstract in *Chem. Abst.* should be consulted. Some of the conclusions are:

1. Azines with normal carbon chain are more rapidly hydrogenated than the *iso*-compounds.
2. With similarly constructed azines, the heavier the radical attached to the nitrogen the slower the hydrogenation.
3. Ketazines hydrogenate more slowly than aldazines.
4. The velocity of reaction does not increase indefinitely with increase in the quantity of catalyst.
5. The solvent is an important factor in determining the speed of hydrogenation. Glacial acetic acid increases the speed. Alcohols (ethyl and methyl) give better speed than ethyl acetate and this than ether. In ether and in ethyl acetate dilution slows the reaction: in acetic acid it has the contrary effect.

2681. Benzylideneazine and *o*-hydrobenzylideneazine, on hydrogenation in glacial acetic acid with colloidal palladium catalyst, yield the primary amines.

2681A. Benzylidene-aniline yields aniline and (?) toluene.

2681B. Benzophenoneanil yields aniline and diphenylmethane. [Rosenmund and Pfankuch, *Ber.*, 1923, **56**, 2258.]

2682. Acetophenone azine to symmetrical dimethylphenylmethyl-hydrazine. Perfectly fresh azine must be used: colloidal platinum catalyst: atmosphere pressure of hydrogen. [Schulze and Lochte, *J. Am. Chem. Soc.*, 1926, **48**, 1030.]

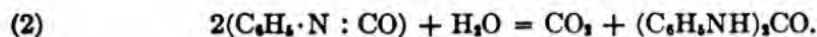
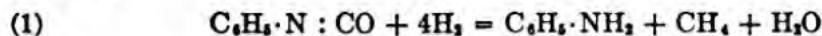
2683. 3-Methylene-2,5-diketopiperazine ("anhydro-glycylserine anhydride") to glycyl-*dl*-alanine anhydride. Acetic acid solution: spongy platinum catalyst.

2684. 3-Methylene-6-methyl-2,5-diketopiperazine to alanine anhydride. Acetic acid solution platinum catalyst. [Bergmann, Miekeley and Kann, 1925, *Z. physiol. Chem.*, **146**, 247.]

2685. Ethyl-carbylamine to methyl-ethyl-amine (with some mono- and di-propyl amines). Gas phase: 160°-170° nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 955.] Tar poisons catalyst.

2686. Methyl-carbylamine, $CH_3 \cdot N : C$, to dimethyl-amine (80 per cent yield). Gas phase: 160°: nickel catalyst. Tarry deposit on catalyst surface reduces activity. [Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 955.]

2687. Phenyl isocyanate hydrogenated over nickel at 190° yields aniline, methane, carbon dioxide and crystals of diphenyl-urea. [Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 825.]



2688. Phenyl-pyroracemic acid to phenylalanine. Liquid phase: palladium catalyst in presence of ammonia. Benzyl-pyroracemic acid to benzylaminocarboxylic acid.

2689. Benzoic acid with palladium catalyst in ammoniacal alcohol gives dibenzylamine: cinnamic aldehyde gives diphenylethylamine: benzophenone gives benzohydrylamine (C_6H_5)₂CH · NH₂. [Knoop and Oesterlin, *Z. physiol. Chem.*, 1927, **170**, 186; *Chem. Abst.*, **22**, 409.]

2690. I. Bases from Carbonyl Compounds.¹⁹ Catalytic reduction of Schiff's bases in acid solution can be effected satisfactorily only with the more stable members of the group, since with less stable compounds the rate of hydrolysis exceeds that of hydrogenation.

¹⁸ *J. Russ. Phys. Chem. Soc.*, 1925, **57**, 487; a full abstract in *Chem. Abst.*, 1926, **20**, 3282.

¹⁹ Skita and Keil, *Ber.*, 1928, **61B**, 1452.

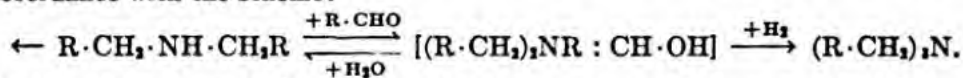
tion. In neutral solution or suspension the absorption of hydrogen is inadequate, but formation of secondary bases occurs readily after addition of ammonia or a primary amine. It is frequently more advantageous to start with a mixture of aldehyde and amine instead of pre-formed Schiff's base. Aldehydes of high molecular weight in presence of ammonia are reduced exclusively to secondary amines, whereas the simpler aldehydes afford tertiary amines. Ketones in presence of ammonia or primary amines give secondary bases.

Cyclohexyl- $\gamma\gamma$ -dimethyloctylideneamine, from citral and cyclohexylamine is converted by hydrogen in the presence of alcohol, acetic acid, and colloidal platinum into cyclohexyl- $\gamma\gamma$ -dimethyloctylamine. In neutral solution, isoamyl- $\gamma\gamma$ -dimethyloctylideneamine, affords isoamyl- $\gamma\gamma$ -dimethyloctylamine. In aqueous suspension in the presence of ammonia, ethyl- $\gamma\gamma$ -dimethyloctylideneamine, yields ethyl- $\gamma\gamma$ -dimethyloctylamine. Methyl- $\gamma\gamma$ -dimethyloctylideneamine affords methyl- $\gamma\gamma$ -dimethyloctylamine in very modest yield.

2691. Hydrogenation of citral in aqueous suspension in presence of colloidal platinum and ammonia gives di- $\gamma\gamma$ -dimethyloctylamine, obtained also by reduction of citral oxime. Heptaldehyde, under similar conditions, yields diheptylamine. Acetaldehyde and propaldehyde or the oximes afford triethylamine and tripropylamine, respectively.

Diisopropylamine is prepared from acetone, while methyl ethyl ketone affords methyl-ethylcarbinol and di-*sec.*-butylamine. Di- α -ethylpropylamine is prepared in about 20 per cent yield from diethyl ketone. Cyclohexanone yields a mixture of cyclohexanone and dicyclohexylamine. Ethyl-*sec.*-butylamine and cyclohexylethylamine are derived from ethylamine and methyl ethyl ketone or cyclohexanone, respectively.²⁰

2692. II.²¹ Ketones react generally with aliphatic amines and ammonia, even in aqueous suspension, giving intermediate *N*-substituted imines which are reduced to secondary amines in the presence of platinum. On the other hand, if nickel is used as catalyst, ketones and ammonia give substantially primary amines, which are also obtained from aldehydes. If, however, the conditions used for nickel are followed (temperature 90°) but the amount of platinum is greatly diminished, the production of primary amines becomes marked, but always subordinate to that of secondary amines. At the atmospheric temperature, secondary amines are produced exclusively. In confirmation, mixtures of acetone, methyl ethyl ketone, diethyl ketone, or cyclohexanone with cyclohexylamine do not form secondary amines in the presence of nickel, whereas they readily do so under the influence of platinum at 90° or at atmospheric temperature. Similarly, benzaldehyde and acetophenone in aqueous suspension are transformed into secondary bases in presence of platinum. Palladium appears to have an action between those of platinum and nickel. The production of tertiary bases from certain aldehydes occurs in accordance with the scheme:



Reduction of diketones in the presence of primary amines affords amino-alcohols in very satisfactory yield; these compounds are also derived from hydroxyaldehydes and hydroxy ketones in presence of bases. The method can be applied in the sugar group.

2693. *N*-isopropylcyclohexylamine, from acetone and cyclohexylamine, *N*-*sec.*-butylcyclohexylamine, from methyl ethyl ketone and cyclohexylamine; *N*- α -ethyl-*n*-propyl-cyclohexylamine, from diethyl ketone; benzyl-diethylamine from benzaldehyde, acetaldehyde, and ethylamine, or benzylethylamine and acetaldehyde; β -cyclohexylaminopentan- γ -ol, from acetylacetone and cyclohexylamine; β -cyclohexylaminopropan- α -ol; *N*-cyclohexylarabinamine, $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CH_2 \cdot NH \cdot C_6H_{11}$, from arabinose and cyclohexylamine, m.p. 135°-137°; *N*-cyclohexylmannamine hydrochloride, m.p. 165°-167°.²²

²⁰ Skita and Koil, *Ber.*, 1928, **61B**, 1452; *Chem. Abst.*, 1928, **23**, 4502; *Brit. Chem. Abst.*, 1928, 1120A.

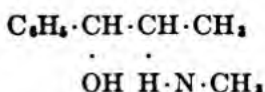
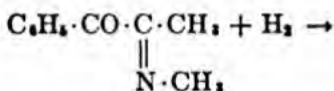
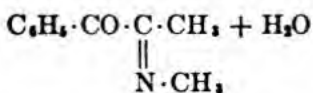
²¹ *Idem*, *Ber.*, 1928, **61B**, 1682.

²² *Idem*, *ibid.*, *Brit. Chem. Abst.*, 1928, 1228A.

2694. Ketones, Aldehydes and Their Ammonia Derivatives to Primary Aliphatic and Cyclic Amines. Ketones, aldehydes, or their ammonia compounds are passed at 100°–200° with hydrogen and ammonia over hydrogenation catalysts (reduced nickel and silica on pumice) preferably with the addition of dehydrating catalysts (aluminum phosphate, alumina) and activators (zinc oxide, magnesium oxide). Cyclo-hexylamine, *n*-butylamine, and isobutylamine are thus obtained together with only insignificant amounts of secondary and tertiary amines.²²

2695. Preparation of *N*-aralkylated Aromatic Amines. Arylideneamines (Schiff's bases) are treated with hydrogen or gases containing hydrogen below 180° in the presence of a catalyst formed from one or two metals of the iron group or their oxides or salts, preferably with addition of a heavy metal not belonging to the iron group, such as copper or its oxide or a salt. The C : N linking is thereby smoothly reduced and an almost quantitative yield of the corresponding *N*-aralkylamine is obtained. For example, *N*-benzal-*p*-phenetidine dissolved in decahydronaphthalene is treated with hydrogen under a pressure of 5 atmospheres at 90°–100° in presence of about 5 per cent of nickel-cobalt-copper catalyst to give *N*-benzyl-*p*-phenetidine, in quantitative yield. *NN*-Dibenzylidene-*p*-phenylenediamine similarly treated gives *NN*-dibenzyl-*p*-phenylenediamine. *N*-Cinnamylidene-*p*-phenetidine treated in hexahydrotoluene with hydrogen under pressure at 100° in presence of a nickel-copper catalyst yields *N*- γ -phenylpropyl-*p*-phenetidine. [J. D. Riedel A.-G., Ger. Pat. 423,132, Mar. 4, 1924. *Brit. Chem. Abst.*, 1926, 771B.]

2696. Amino-alcohol Synthesis: Ephedrine. Phenyl methyl diketone and methylamine are dissolved in alcohol and the solution mixture is catalytically hydrogenated under pressure.



The method is a general one for synthesis of amino alcohols. [Manske and Johnson, see para. 3067.] Phenylpropanol amine, *p*-tolyl-propanol amine, and *o*-hydroxyphenyl propanol amine have been prepared by reduction of the corresponding isonitroso ketones ($\text{Ar} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{HNO}_2$) in presence of palladized charcoal. These products resemble ephedrine in their pharmacologic properties. [Hartung and Munch.] β -Methyl-imino- α -phenylpropanone to *dl*-ephedrine. Alcohol solution: platinum catalyst. [Manske and Johnson, *J. Am. Chem. Soc.*, 1929, 51, 580.]

2697. Pyruvic acid (alpha-ketopropionic acid) to alanine (alpha-aminopropionic acid.) Pyruvic acid 1 mol, ammonia 2 mols, stirred in a hydrogen atmosphere for several days with a colloidal platinum catalyst and starch as protective colloid. [Aubel and Bourguet, *Compt. rend.*, 1928, 186, 1844.]

2698. 2-Methylbenzisooxazol to 2-hydroxy-5-methylacetophenone. Acetic acid solution: palladium catalyst. When the solvent is anhydrous ether the ketimine is formed. [Lindemann and Pickert, *Ann.*, 1927, 456, 275.]

2699. 2-Phenyl-1:4-pyrone to phenylcarbamyldihydrazone. Colloidal palladium catalyst. [Borsche and Peter, *Ann.*, 1927, 453, 148.]

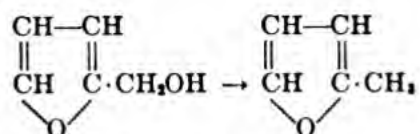
²² *Brit. Pat.* 265,960, Feb. 7, 1927, to the I. G.; *Brit. Chem. Abst.*, 1928, 360B.

CHAPTER XXVII

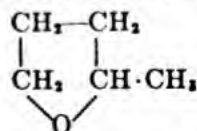
HYDROGENATION OF HETEROCYCLIC COMPOUNDS

I

2700. Furfural (pyromucic aldehyde) can be reduced to furyl alcohol in the gas phase at 190° over nickel catalyst. Pushed farther the hydrogenation of the furyl alcohol gives methyl furfurane:



In turn the α methyl-furfurane adds 2H₂ and tetrahydro- α methyl-furfurane results.



On continuing the operation the ring is opened up and, first, methyl-propyl-ketone and finally methyl-propyl-carbinol (pentanol) are formed. [Padoa and Ponti, *Lincei*, 1906, **15** (2), 610, *Chem. Centr.*, 1907 (1), 570.]

2701. Furfural is treated in the vapor phase over a catalyst with a large excess of hydrogen for the production of furyl alcohol. The proportion of methylfuran formed increases with rise in temperature.¹

2702. Furfural: Hydrogenation to Tetrahydrofurfural.² When direct hydrogenation of furfural is practised, tetrahydrofurfural is not obtained; the aldehyde group CHO is always attacked.^{3a} It was, therefore, sought to protect this group. Two methods of hydrogenation were tried: (1) of the diethyl acetal; (2) of the diacetate. The second was completely successful, the first less so, there being in the product a considerable quantity of impurities as well as some unchanged furfural. Details of the preparation of these two bodies are given in the original paper, and in the abstract cited as well as those of the purification of the tetrahydrofurfural. The conditions of the hydrogenation were: (1a) 7 g. of the diethyl acetal with 0.09 colloidal platinum, required fifty-five hours for complete hydrogenation, the catalyst being twice activated with air. (1b) 6 g. of the diethyl acetal, dissolved in 25 cc. ether or alcohol, with 2.4 g. palladinized charcoal (0.12 g. palladium) took six hours, absorbing a little more hydrogen than the theoretical quantity for tetrahydrofurfural. The product, as we have said, contained some furfural. (2a) 5 g. diacetate in acetic acid, with 0.3 g. platinum sponge was completely hydrogenated in fourteen hours, the catalyst being reactivated three times. (2b) With palladinized charcoal (0.15 g. palladium) the hydrogenation was complete in five hours in

¹ French Pat. 639,756, Jan. 31, 1927, to Soc. Anon. des dist. des Deux-Sèvres.

² Scheibler, Sotscheck and Friese, *Ber.*, 1924, **57B**, 1443; *Chem. Abst.*, 1925, **19**, 278.

^{3a} See Figures 25b and 25c, pages 183 and 210 respectively. Pierce and Parks, *J. Am. Chem. Soc.*, 1929, **51**, 3384.

acetic acid and in three and three-quarter hours in ether. The ether requires special purification by washing with solution of sodium hydroxide and with alkaline permanganate and drying, first with calcium chloride and finally over sodium. The hydrogenation must not be interrupted (except for the reactivations of the catalyst) and, therefore, work should be done with small quantities (e.g., 5 g.) at a time. The catalyst may be regenerated by washing with alcohol and ether, heating in carbon dioxide two hours at 140°–150° C. and cooling in carbon dioxide.

2703. In alcoholic solution at 3 atmospheres total pressure with platinum oxide catalyst, after 1 molecule of hydrogen is absorbed, furyl alcohol, in quantitative yield, is obtained. On continuation of the hydrogenation there results a mixture of tetrahydrofuryl alcohol, pentane-1, 2-diol (?), pentane-1, 5-diol and ammonia. The tetrahydrofuryl alcohol is the chief product. Ferrous chloride very markedly promotes this hydrogenation. [Kaufmann with Adams, *J. Am. Chem. Soc.*, 1923, **45**, 3029.]

2704. Hydrogenation of Furan Derivatives. Kariyone applied four methods of catalytic hydrogenation, viz., platinum-black, colloidal platinum solution, palladium on barium sulphate and colloidal palladium solution. The furan derivatives used were: (1) Those containing $-\text{CH}_2-$ or $-\text{CH}=\text{}$ at the α -position of the furan nucleus (furfurethylene, furylacrylic acid, furfuralacetone, furylphenylmethane, and furyl alcohol). (2) Those having $-\text{CO}-$ group at the α -position (furyl methyl ketone, furyl phenyl ketone, furin, furil and furylethyl ether). (3) Furfural and its derivatives (furfural, furfural di-ethyl acetal and furfurylidene diacetate). (4) Furancarboxylic acid and its derivatives (pyromucic acid, ethyl pyromucate, pyromucic amide, furfuronitril, β -(?)-nitropyromucic acid, dehydromucic acid, dimethyl dehydromucate and methylfuran-carboxylic acid. The conclusions may be summarized as follows: The members of group (1) are the most easily hydrogenated, next (2) and $-\text{CO}_2\text{H}$ acid derivatives are rather difficult to be reduced. The dehydromucic acid can be easily reduced by Na-Hg, but difficultly by catalytic hydrogenation. In (3), the diethyl ester is the easiest to be reduced, furfural being the most difficult. When 1 molecule hydrogen was added to those having a side chain with a double bond, Kariyone found that furfurethylene gave a large amount of the original substance and a trace of the 6-hydro derivative, while furylacrylic acid gave, quantitatively, furylpropionic acid.³

2705. Alkyl furyl carbinols hydrogenated with the Voorhees-Adams platinum oxide catalyst yielded a mixture of (a) isomeric alkyl tetrahydrofuryl carbinols, (b) isomeric alkyl *n*-propyl-1,2-glycols, (c) alkyl 1,5-glycols, (d) alkyl butyl carbinols. Alcoholic solutions were used.

2706. Ethyl-furyl carbinol gave: heptanol-3, ethyl-tetrahydrofuryl carbinol (apparently a mixture of the 2 isomers), heptanediol-3, 4 (1 isomer, one solid, the other liquid), heptanediol-1, 5.

2707. *n*-Butyl-furyl carbinol gave: dibutyl carbinol, butyl-tetrahydrofuryl carbinol, nonanediol-4, 5 (2 isomers, one solid, the other liquid). [Pierce with Adams, *J. Am. Chem. Soc.*, 1925, **47**, 1098.]

2708. Furyl-ethyl-carbinol to tetrahydrofuryl-ethyl-carbinol. Gas phase: 175° : nickel catalyst. [Douris, *Compt. rend.*, 1913, **157**, 722.]

2709. Furfuralacrolein to furylpropylalcohol and by further absorption of hydrogen to tetrahydrofurylpropyl alcohol and a heptane-diol. Alcoholic solution: platinum oxide-platinum-black catalyst: a little ferrous sulphate as promoter.

If the reduction was carried out in the presence of ferrous sulphate and zinc sulphate, the reaction stopped at the absorption of one molecular equivalent of hydrogen and pure furylallyl alcohol was obtained. [Bray and Adams, *J. Am. Chem. Soc.*, 1927, **49**, 2101.]

2710. Alpha-furfurylamine to tetrahydrofurfurylamine. Glacial acetic acid solution: palladinized animal charcoal catalyst. [Williams, *Ber.*, 1927, **60B**, 2509.]

2711. Furfural-oxime to tetrahydro-furfural oxime. Absolute ether solution: palladinized animal charcoal catalyst. [*Ibid.*]

³ Kariyone, *J. Pharm. Soc., Japan*, 1925, No. 515, 1: from *Chem. Abst.*, 1926, **20**, 412.

2712. Rupture of Furane Nucleus. Attempted hydrogenation of furylethylamine, with a platinum oxide catalyst, resulted in rupture of the ring and the formation of γ -hydroxyhexylamine. [Takamoto, *J. Pharm. Soc., Japan*, 1928, **48**, 366.]

2713. Furylpropylamine (with ferrous chloride promoter) gave almost quantitatively tetrahydrofurylpropylamine. On further hydrogenation of this compound fission of the ring occurred with formation on η -hydroxyheptyl amine. [*Ibid.*, 686; *Chem. Abst.*, 1929, **23**, 387.]

2714. Zanetti [*J. Am. Chem. Soc.*, 1928, 1821] stated that α -tetrahydrofurfuryl alcohol would soon be available on a commercial scale from the catalytic reduction of furfural. This has now been realized.

2715. Trickey uses tetrahydrofurfuryl alcohol, made by catalytic hydrogenation, as a solvent in nitrocellulose lacquers.⁴

2716. Pyrrole to pyrrolidine, C_4H_5N . Gas phase : 180° - 190° : nickel catalyst : 25 per cent yield with some hexahydroindoline. [Padoa, *Gazz. Chim. Ital.*, 1906, **36** (2), 317.]

2717. Pyrrole adds $2H_2$ to form pyrrolidine when hydrogenated in the presence of platinum-black. [Willstätter and Hatt, *Ber.*, 1912, **45**, 1371.]

2718. *N*-methylpyrrole to *N*-methylpyrrolidine. Voorhees-Adams platinum oxide catalyst with usual technique. 8.1 g. *N*-methylpyrrole in 40 cc. glacial acetic acid, 0.5 g. catalyst, slight plus pressure of hydrogen : 75 per cent yield. [Wibaut, *Rec. trav. chim. Pays-bas*, 1925, **44**, 1101.]

2719. 1-Methylpyrrole to 1-methylpyrrolidine. By shaking 1-methylpyrrole in acetic acid solution with hydrogen for forty-one hours under a pressure of 20 cm. of water, successive small quantities of platonic oxide being added as a catalyst, a 74 per cent yield of 1-methylpyrrolidine is obtained. [Wibaut, *Rec. trav. chim. Pays-bas*, 1925, **44**, 1101.]

2720. Pyrrole aldehydes to pyrrole alcohols. Alcohol solution.

Were prepared : 2, 5-dimethyl-3-carbethoxy-4-hydroxy-methylpyrrole, 2, 4-dimethyl-3-carbethoxy-5-hydroxy-methylpyrrole, 2, 4-dimethyl-5-carbethoxy-3-hydroxypyrrole. Catalytic reduction in acetic acid gave the methane derivative directly. [Fischer and Stern, *Ann.*, 1925, **446**, 229.]

2721. Ethyl 3-vinyl-2-methyl-4-ethylpyrrole-5-carboxylate to ethyl 2-methyl-3 : 4-diethylpyrrole-5-carboxylate. Platinum-black catalyst. [Fischer and Stangler, *Ann.*, 1927, **459**, 53.]

2722. 5-Aldehyde-2-methylpyrrole-3-carboxylic acid (semicarbazone) to 5-(3-carbethoxy-2-methylpyrrol)-carbinol, and formaldehyde. Platinum catalyst.

2723. Catalytic reduction of the ethyl ester of the acid in glacial acetic acid yields di-5-(3-carbethoxy-2-methylpyrrol) methane. [Fischer and Schubert, *Z. physiol. Chem.*, 1926, **155**, 72.]

2724. Hemin to monohydrohemin. Sodium hydroxide solution : palladium-charcoal or platinum oxide catalyst.

2724A. Hemin to dihydrohemin. Pyridine and chloroform solution : same catalyst.

2724B. Hemin to perhydrohemin. Piperidine and chloroform solution : same catalyst. [Kuhn, Braun, Seyffert and Furter, *Ber.*, 1927, **60B**, 1151; Cf. Fischer and Walter, *Ber.*, 1927, **60B**, 1987.]

2725. The hydrogenation of hemin, dihydrohemin, and mesohemin, in various solvents⁵ and with various catalysts⁶ is detailed in an article by Kuhn and Seyffert, *Ber.*, 1928, **61B**, 2509-2516.

2726. Porphyrin, mesoporphyrin, their hydrochlorides and dimethyl esters were also hydrogenated. [*Ibid.*]

⁴ U. S. Pat. 1,703,697, Feb. 26, 1929 (assigned to Quaker Oats Co.).

⁵ $N/_{10}$ soda, chloroform and pyridine for the hemins; glacial acetic acid for the porphyrins.

⁶ Pd-norit, Pd-charcoal, Pd-BaSO₄, Pd-bone charcoal, Pd-asbestos, Adams' platinum oxide-platinum-black.

2727. Catalytic Hydrogenation of Hemateric Acid and Hemin.⁷ Hemateric acid in acetic acid solution is catalytically hydrogenated to a porphyrin not distinguishable from mesoporphyrin. The maximum amount of hydrogen absorbed is equivalent to 6 atoms of hydrogen per mol of hemateric acid; no decolorization occurs. Mesoporphyrin solutions absorb hydrogen irregularly, and are not decolorized. Appreciable hydrogenation of hemin occurs in acid solution with the formation of mesohemin and mesoporphyrin. In alkaline solution approximately 6 atoms of hydrogen are absorbed per mol of hemin, but spectroscopical examination reveals no mesohemin.⁸

2728. Alcohols of the pyrrolidine series are made by treating pyrroles with alcohol groups in a side chain, in acid solution, with hydrogen in the presence of a catalytic metal of the platinum group, preferably under pressure. The resulting alcohols are applied in pharmacy.⁹

2729. 4-Carboxy-1 : 1-dimethyl-2-methylenepyrrolidinium bromide to 4-carboxy-1 : 1 : 2-trimethylpyrrolidinium bromide. Palladium catalyst. [Mannich and Gollasch, *Ann.*, 1927, **453**, 177.]

2730. *N*-dimethyl- β -ketopyrrolidinium chloride to *N*-dimethyl- β -hydroxy-pyrrolidinium chloride. Skita (shaking) apparatus : platinum sponge catalyst : 2 atmospheres plus pressure hydrogen. [Mannich and Gollasch, *Ber.*, 1928, **61B**, 263.]

2731. 2-Methylene-*N*-dimethylpyrrolidinium chloride to 2-methyl-*N*-dimethylpyrrolidinium chloride. Colloidal palladium or nickel catalyst. [von Braun and Teuffert, *Ber.*, 1928, **61B**, 1092.]

2732. Skita and Brunner¹⁰ found that pyridine was readily reduced to piperidine in dilute hydrochloric acid solution by hydrogen in presence of colloidal platinum, but that traces of pentane were produced at the same time. The hydrogenation of α -picoline, α -lutidine, and 2,4,5-collidine proceeded with greater difficulty, but good results were obtained in acetic acid solution at 25°–45° C. under an excess pressure of 3 atmospheres. α -Phenylquinolinecarboxylic acid was reduced to tetrahydrophenylquinolinecarboxylic acid when treated in dilute glacial acetic acid solution at 50°–60° C. with hydrogen under an excess pressure of 1 atmosphere, in presence of a platinum catalyst, while the decahydro-compound was obtained by working under a pressure of 3 atmospheres, and using a larger quantity of catalyst. The tetrahydro-compound is crystalline and melts at 218° C., while the decahydro-derivative is amorphous, melting at 330° C. (with decomposition). The hydrogenation of the cinchona alkaloids, although presenting greater difficulty, was also effected. Thus quinone, or dihydroquinone, absorbed 3 or 6 mols. of hydrogen, according to the duration of treatment, being converted into hexahydrocinchonidine, m.p. 206° C., and dodecahydrocinchonidine, m.p. 104° C. The same hexahydrocinchonidine was also obtained by catalytic reduction of dihydrocinchonidine. Similarly by the hydrogenation of quinidine and cinchonine a hexahydrocinchonine of the formula $C_{19}H_{25}N_2O$, m.p. 241° C., was obtained.¹¹

2733. Pyridine and Quinoline. The influence of different catalysts in the hydrogenation of pyridine and quinoline by Ipatiev's method has been intensively studied by Sadikov and Mikhailov.¹² For the elaborate details of pressure, temperature, rates of absorption of hydrogenation, and the results of fractionation of the products, the original articles or the (full) abstracts must be consulted.

2734. The catalysts used for pyridine were platinized asbestos, palladium asbestos, iridium and osmium on asbestos. The catalytic power was found to increase with the affinity for oxygen in the order: platinum, palladium, iridium, osmium. The chief prod-

⁷ Papendieck, *Z. physiol. Chem.*, 1927, **169**, 59.

⁸ *Brit. Chem. Abst.*, 1927, 109A.

⁹ Ger. Pat. 283,333, Oct. 21, 1913, to Bayer & Co.; *Chem. Abst.*, 1915, **9**, 2569.

¹⁰ *Ber.*, 1916, **49**, 1597–1605.

¹¹ *J.S.C.I.*, 1916, **35**, 1033.

¹² *J. Russ. Phys. Chem. Soc.*, 1927, **58**, 527; *Chem. Abst.*, 1927, **21**, 3364; *J. Chem. Soc.*, 1928, 438; *Chem. Abst.*, 1927, **21**, 3364; *Ber.*, 1928, **61B**, 421; *Chem. Abst.*, 1928, **22**, 1974. The *Berichte* article deals with the two alkaloidal by-products of the hydrogenation of pyridine.

uct of the hydrogenation of pyridine was piperidine (70 per cent). With 20 per cent osmium-asbestos the by-products were found to contain two high boiling compounds of an alkaloidal character, $C_9H_{15}N$, probably *N*-methyl-beta-propyl-piperidine (*N*-methylconiine) and α, α' -dimethyl-beta-propyl-*N* (*N'*-dipiperidyl), $C_{11}H_{20}N_2$.

2735. The best catalyst for quinoline was found in an association of osmium (20 per cent on asbestos) and ceric oxide. Ceric oxide alone (20 per cent on asbestos) will "facilitate" the hydrogenation of quinoline, giving a yield of 88 per cent tetrahydroquinoline; but for the hydrogenation of pyridine, naphthalene and benzene, and for the further hydrogenation of tetrahydro- and hexahydroquinoline, it must be associated with a catalytic metal. Ceric oxide has a decided retarding action on the hydrogenation of pyridine.

2736. Catalytic Hydrogenation of Pyridine. Pyridine was hydrogenated in an open tube, and by Ipatiev's method under pressure in the presence of catalysts prepared by Zelinsky's method.¹³ In an open tube at 150°, with 40 per cent platinized asbestos, the hydrogenation was very slow (300 hours). The product was fractionated and the refractive indices and densities were determined. No amylamine was isolated, but 60 per cent of tetrahydro-pyridine, together with condensation products of higher boiling-point resulted. With 20 per cent platinized asbestos at 200°, hydrogenation by Ipatiev's method was very slow: after six hours 6.6 per cent, after twenty-four hours 7.8 per cent; at 250° after sixteen hours about 20 per cent. Palladized asbestos (20 per cent), under the same conditions, gave a 70 per cent yield after nineteen hours, while 20 per cent iridized asbestos gave complete absorption of hydrogen after twelve hours. With 20 per cent osmized asbestos, absorption is complete after six hours at 240°, and a 30 per cent yield of condensation products of higher boiling-point is obtained; 5 per cent and 1 per cent osmium catalysts also give complete absorption. The efficiency of the catalysts is in the order of their oxidizability: a colloidal suspension of the metal in pyridine may be formed which adsorbs oxygen and causes the hydrogen molecule to dissociate into atoms, which then add on to the unsaturated compound. The possible influence of traces of water is also mentioned. [Sadikov and Mikhailov, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 527; *Brit. Chem. Abst.*, 1927, 253A.]

2737. Pyridine to piperidine. Liquid phase: colloidal palladium catalyst. [Skita and Meyer, *Ber.*, 1912, **45**, 3587.] The same hydrogenation may be effected in presence of a gum-arabic protected colloidal platinum catalyst. [*Ibid.*, 3589.] In the gas phase, over nickel at 120°–220°, pyridine is not hydrogenated to piperidine: the ring is slowly attacked and opened with production of very little amylamine. [Sabatier and Mailhe, *Compt. rend.*, 1907, **144**, 784.]

2738. The homologs of pyridine take up $3H_2$ when hydrogenated in acetic acid solution with a gum arabic protected colloidal platinum catalyst, under atmospheric pressure or under 2–3 atmospheres. [Skita and Brunner, *Ber.*, 1916, **49**, 1597.]

2739. Pyridine is very readily hydrogenated to piperidine in the presence of platinized asbestos (40 per cent) at 150°. The catalyst does not become poisoned, since it retains its ability to cause the hydrogenation of benzene. At about 250° it smoothly effects the dehydrogenation of piperidine, but, after use, it is no longer capable of bringing about the reduction of benzene or pyridine or the dehydrogenation of cyclohexane. Palladized asbestos is a still more effective agent for the hydrogenation of pyridine at 150°; after use, however, it is found to have lost all activity towards benzene. It readily causes the dehydrogenation of piperidine, but not of cyclohexane at 250°; after use, it is incapable of effecting hydrogenation.

2739A. The preparation of the highly active catalyst is effected in the following manner. Asbestos, which has been washed with acid and ignited, is soaked in a concentrated, faintly acid solution of platinum or palladium chloride at the temperature of boiling water and subsequently immersed in cold formaldehyde solution (35–40 per cent). It is then treated with concentrated sodium hydroxide solution (40–50 per cent), initially at 0° and finally on the water-bath. The product is washed thoroughly with

¹³ Cf. para. 2739A.

water, immersed in dilute acetic acid solution, and again washed until the filtrate is neutral in reaction. It is dried for a short period at 110°. [Zelinsky and Borisoff, *Ber.*, 1924, **57B**, 150; *J. Chem. Soc. Abst.*, 1924, i, 241.]

2740. Pyridine cannot be reduced directly, or in a solvent with platinum-oxide platinum-black. If it is converted to the hydrochloride the reduction goes smoothly. Comparison of the reduction of pyridine hydrochloride with a number of pyridonium chlorides indicated that the rate of reduction is as follows, the slowest being given first: Pyridine hydrochloride, pyridonium ethyl chloride, butyl chloride, hexyl chloride, carbethoxy-methyl chloride, beta-hydroxy ethyl chloride, gamma-hydroxy ethyl chloride.¹⁴

2741. In most solvents pyridine poisons the platinum-black. For the reduction of the hydrochloride absolute ethanol is the best and glacial acetic acid the next best solvent. Water inhibits the reduction. With 0.1 mole pyridine hydrochloride, 150 cc. solvent, and 0.15 g. catalyst the reduction is complete in seven hours. The use of 0.5 g. catalyst cuts this time to thirty minutes. Increase of temperature to 50° also accelerates the reaction. Pyridinium salts gives hexahydro-, quinolinium salts tetrahydro-derivatives. [Hamilton and Adams, *J. Am. Chem. Soc.*, 1928, **50**, 2260.]

2741A. Pyridine in liquid state passed over nickel at 180° C. under 20 atm. hydrogen pressure, yields piperidine and a little tetrahydropyridine, no amylamine.^{14a}

2742. 2-β-Hydroxy-*n*-propylpyridine-methosulphate to 1-methyl-2-β-hydroxy-*n*-propylpiperidine. Platinum-platinum oxide catalyst.

2-β-Hydroxy-*n*-propylpyridine to 2-β-hydroxy-*n*-propylpiperidine. (These compounds are related to iso-pelletierine.) [Meisenheimer and Mahler, *Ann.*, 1928, **462**, 301.]

2743. β-Pyridyl γ'-methylaminopropyl ketone to the alcohol. Palladium charcoal catalyst. (A new synthesis of nicotine.) [Späth and Bretschneider, *Ber.*, 1928, **61B**, 327.]

2744. Ethyl 1 : 2 : 6 : 1' : 2' : 6'-hexamethyl-4 : 4'-diisobutyltetrahydrodipyridyl-3 : 5 : 3' : 5'-tetracarboxylate to ethyl 1 : 2 : 6-trimethyl-4-isobutyl-1 : 2-dihydropyridine-3 : 5-dicarboxylate. Colloidal palladium catalyst. This latter compound on hydrogenation in acetic acid solution with spongy platinum yields the corresponding tetrahydro compound. [Mumm and Ludwig, *Ber.*, 1926, **59B**, 1605.]

2745. Dipiperidyls.¹⁵ The isomeric dipiperidyls conveniently obtained by hydrogenating the corresponding dipyridyls, using a platinum oxide-platinum-black catalyst in aqueous or alcoholic hydrochloric acid. Products of partial reduction were not formed. The following are described: 4 : 4'-dipiperidyl, m.p. 172°; 2 : 2'-dipiperidyl di-phenyl-thiourethane, m.p. 178°; 3 : 3'-dipiperidyl, m.p. 105°, b.p. 282°; and 3 : 4l-dipiperidyl, m.p. 159°, b.p. 270°.¹⁶

2746. Methylpiperidines.¹⁷ 3-Methylpiperidine-3-methylpyridine (β-picoline) was prepared from glycerol ammonium phosphate and phosphorus pentoxide, according to the method of Schwarz. [*Berichte*, 1891, **24**, 1676.] The hydrochloride was prepared and reduced catalytically, using the same procedure as that employed for the preparation of 3-carbethoxypiperidine. The 3-methylpiperidine so obtained boiled at 123°-126°.

2-Methylpiperidine-2-methylpyridine (α-picoline) was isolated from the picoline fraction of coal-tar bases which boiled at 127-132° by the method of Heap, Jones and Speakman (*J. Am. Chem. Soc.*, 1921, **43**, 1936). It was reduced in a manner similar to that used for 3-methylpyridine. The 2-methylpiperidine boiled at 114°-116°.

2746A. α-3-Methylpiperidinoacetone (hydrochloride) to α-3-methylpiperidino-β-propyl alcohol (hydrochloride). Alcohol solution : platinum catalyst. [Thayer and McElvain, *J. Am. Chem. Soc.*, 1928, **50**, 3348.]

¹⁴ Hamilton and Adams, *J. Am. Chem. Soc.*, 1928, **50**, 2260; *Chem. Abst.*, 1928, **22**, 3165.

^{14a} Brit. Pat. 309,300, Mar. 31, 1928 to Techn. Res. Wks., Ltd. and Lush.

¹⁵ Smith, *J. Am. Chem. Soc.*, 1928, **50**, 1936.

¹⁶ *Brit. Chem. Abst.*, 1928, 1025A.

¹⁷ McElvain, *J. Am. Chem. Soc.*, 1927, **49**, 2837.

2746B. α -3-Methylpiperidino-butane- γ -one (hydrochloride), hydrogenated and benzoylated yields α -3-methyl-piperidino- γ -benzoyloxybutane (hydrochloride). [*Ibid.*]

2747. 1-Methyl-3-carbethoxy-4-piperidone (hydrochloride) to 1-methyl-3-carbethoxy-4-hydroxypiperidine. 15 g. in 75 cc. absolute alcohol : Voorhees-Adams' platinum oxide catalyst : 2 atmospheres pressure : fifty hours' shaking. [McElvain, *J. Am. Chem. Soc.*, 1924, **46**, 1721.]

2748. By the same method the 1-alkyl-3-carbethoxy-4-hydroxy-piperidines were prepared from the corresponding 1-alkyl-3-carbethoxy-4-piperidone hydrochlorides. The alkyl radicles were: ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *sec*-butyl, *n*-amyl and *iso*-amyl. Only the ethyl and the two propyl derivatives were isolated as the others decomposed on distillation. [McElvain, *J. Am. Chem. Soc.*, 1926, **48**, 2179.]

2749. Similarly the 1-alkyl-3-carbethoxy-4-piperidyl *p*-aminobenzoate (dihydrochlorides) were obtained from the 1-alkyl-3-carbethoxy-4-piperidyl *p*-nitrobenzoate (hydrochlorides). The reduction was complete in five minutes. The alkyl radicles were: methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl and *iso*-amyl. These products are of pharmacologic importance on account of their local anaesthetic properties. [McElvain, *J. Am. Chem. Soc.*, 1926, **48**, 2239.]

2750. 3-Carbethoxy-1-alkyl-4-piperidones as hydrochlorides hydrogenated in presence of platinum oxide yield the corresponding 4-hydroxy-3-carbethoxy-1-alkylpiperidines. (These yield powerful local anaesthetics of low toxicity.) [McElvain, *J. Amer. Chem. Soc.*, 1926, **48**, 2179.]

2751. 1-(3-Methylpiperidino)-propanone hydrochloride to 1-(3-methylpiperidino)-propanol hydrochloride. Alcohol solution : Adams' platinum-oxide platinum-black catalyst (0.3 g. catalyst to 15.5 g. ketone) : three and one-half to four hours.

2752. 1-(3-Methylpiperidino)-butanone-3-hydrochloride to 1-(3-methylpiperidino)-butanol. As above. [Thayer and McElvain, *J. Am. Chem. Soc.*, 1928, **50**, 3351-3352.]

2753. Unsaturated γ -Ketonic Amines: Hydrogenation.¹⁸ The following results are reported:—

2753A. ϵ -Piperidino- α -phenyl- Δ^{α} -pentene- γ -one to ϵ -piperidino- α -phenylpentane- γ -one. Palladium charcoal catalyst.

2753B. ϵ -Diethylamino- α -phenyl- Δ^{α} -pentene- γ -one to ϵ -diethylamino- α -phenylpentane- γ -one.

2753C. ϵ -Piperidino- α -3 : 4-methylenedioxyphenyl- Δ^{α} -pentene- γ -one to ϵ -piperidino- α -3 : 4-methylenedioxyphenyl-pentane- γ -one. Glacial acetic acid : palladium-charcoal catalyst.

2753D. ϵ -Piperidino- α -3 : 4-dimethoxyphenyl- Δ^{α} -pentene- γ -one to ϵ -piperidino- α -3 : 4-dimethoxyphenylpentane- γ -one.

2753E. ϵ -Diethylamino- α -3 : 4-methylenedioxyphenyl- Δ^{α} -pentene- γ -one to ϵ -diethylamino- α -3 : 4-methylene dioxypentylpentane- γ -one.

2753F. ϵ -Piperidino- α -*p*-anisyl- Δ^{α} -pentene- γ -one to ϵ -piperidino- α -*p*-anisylpentane- γ -one.

2753G. ϵ -Diethylamino- α -3 : 4-dimethoxyphenyl- Δ^{α} -pentene- γ -one was obtained but in poor yield and (apparently) was not hydrogenated.

2754. 3-Piperidinomethyl-2-hexenone hydrobromide to 3-piperidinomethyl-2-hexanone hydrobromide. In water: palladium-charcoal catalyst. [Mannich and Gollasch, *Ber.*, 1928, **61B**, 263.]

2755. α -Propenylpyridine hydrogenated in presence of colloidal platinum gives a product from which conine may be obtained by the action of sodium and ethanol. [Koller, *Monatsch.*, 1926, **47**, 393.]

2756. Pyridine-carboxylic acids to piperidinic acids. Liquid phase : colloidal platinum catalyst. [Hess and Liebrandt, *Ber.*, 1917, **50**, 385.]

2757. 1 : 4-Dimethyltetrahydropyridine-3-carboxylic acid to 1 : 4-dimethylpiperidine-3-carboxylic acid. Palladium-animal charcoal catalyst. [Mannich and Stein, *Arch. Pharm.*, 1926, **264**, 77.]

¹⁸ Mannich and Schütz, *Arch. Pharm.*, 1927, **265**, 684.

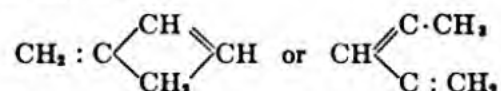
2758. 3-Acetyl-1 : 4-dimethyl-tetrahydropyridine to 3-acetyl-1 : 4-dimethyl-piperidine. In acid solution : palladium-animal charcoal catalyst.

2759. Hydrogenation with Rupture of Molecule. Triphenylpyridinephenylimine in methanol solution was shaken with platinum-black and hydrogen. The reaction was very rapid. Triphenyl-2.4.6-pyridine (75 per cent of theoretical) and aniline were produced. [Schneider and Weiss, 1928, *Ber.*, **61B**, 2448.]

2759A. Similarly: methyl-2-diphenyl-4,6-pyridinephenylimine was split yielding aniline and methyl-2-diphenyl-4,6-pyridine. [Dilthey, *J. prakt. Chem.*, 1916 (2), **94**, 75.]

2760. *N*-dimethylpiperidine to alpha-dimethylamino-*n*-pentane. (v. Braun and Teuffert, *Ber.*, 1928, **61B**, 1092.)

2761. Pirylyene, probably either:



is the ultimate product of the Hofmann degradation of piperidine. It readily takes up 2 molecules of hydrogen on catalytic hydrogenation. [*Ibid.*]

2762. Piperidyl Compounds. Methyl nicotinate to methyl hexahydronicotinate. Absolute ethanol-acetic acid solution: Adams' platinum-black catalyst.

2762A. Derivatives of this hexahydronicotinate obtained by condensation with (1) beta-bromoethyl para-nitrobenzoate and (2) gamma-bromopropyl para-nitrobenzoate, yield on catalytic hydrogenation (1) beta- (3-carbomethoxy-piperidyl) ethyl para-nitrobenzoate hydrochloride and (2) gamma- (3-carbomethoxy-piperidyl) propyl para-aminobenzoate hydrochloride. [Barnes and Adams, *J. Am. Chem. Soc.*, 1927, **49**, 1307.]¹⁹

2762B. Beta-hydroxyethylpyridinium chloride to *N*-beta-hydroxyethylpiperidine. [*Ibid.*]

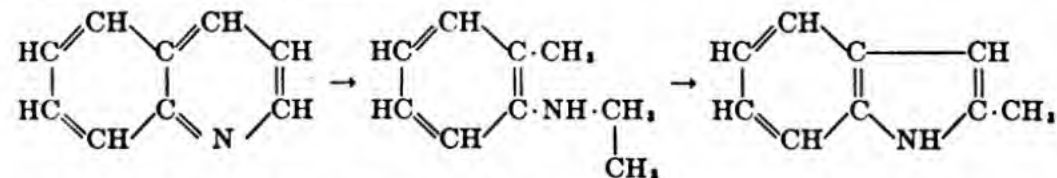
2762C. Gamma-hydroxypropylpyridinium chloride to *N*-beta-hydroxyethylpiperidine. [*Ibid.*]

2762D. Beta-piperidylethyl para-nitrobenzoate hydrochloride to beta-piperidylethyl para-aminobenzoate hydrochloride. [*Ibid.*]

2762E. Gamma-piperidylpropyl para-nitrobenzoate hydrochloride to gamma-piperidylethyl para-aminobenzoate. [*Ibid.*]

2763. Nicotinic acid hydrochloride to nicotinic acid hydrochloride, with Voorhees-Adams' platinum oxide catalyst. 10 g. hydrochloride in 150 cc. water plus 1.0 g. catalyst : initial pressure 2.75 atmospheres : time, two hours. [Voorhees with Adams, *J. Am. Chem. Soc.*, 1922, **44**, 1405.]

2764. Quinoline to α -methyl-indol. Gas phase : 200° : nickel catalyst. In two stages: first, the ring opens and ethyl-orthotoluidine results, then the ring closes again and α -methyl-indol is produced:



[Padoa and Carughi, *Lincei*, 1906, **15**, 113; *Chem. Centr.*, 1906 (2), 1011.]

2764A. At 160°-190° tetrahydroquinoline is produced in 70 per cent yield. [Darzens, *Compt. rend.*, 1909, **149**, 1001.]

¹⁹ Cf., Sandborn and Marvel, *J. Am. Chem. Soc.*, 1928, **50**, 563. For hydrogenation of 1-alkyl-4-piperidyl-*p*-nitrobenzoate hydrochlorides to the corresponding aminobenzoate hydrochlorides see Bolyard and McElvain, *J. Am. Chem. Soc.*, 1929, **51**, 922. In the same article is described the preparation of 1-alkyl-4-piperidyl benzoate hydrochlorides by reduction of the piperidone hydrochlorides.

2764B. At 130°–140° decahydroquinoline may be obtained. [Sabatier and Murat, *Compt. rend.*, 1914, **158**, 309.]

2765. Hydrogenated by Ipatiev's method, with "nickel oxide" catalyst, quinoline gives an almost quantitative yield of decahydroquinoline. In this case there is an intermediate formation of tetrahydroquinoline. [Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 491; *Chem. Centr.*, 1908 (2), 1098.]

2766. The same end-product, decahydroquinoline, is obtained by hydrogenating quinoline in the liquid phase, with either colloidal palladium or colloidal platinum (gum arabic protective) catalyst; with the platinum catalyst there is intermediate formation of tetrahydroquinoline. [Skita and Meyer, *Ber.*, 1912, **45**, 3589 and 3587.]

2767. Hydrogenation of quinoline in presence of platinum-black yielded two decahydroquinolines, one liquid and the other solid. The liquid isomer was also obtained in 10 per cent yield by hydrogenation in vapor phase with Sabatier's technique. [Fujise, *Sci. Papers Inst. Phys. Chem. Res.*, Tokyo, 1928, **8**, 161. Cf. Hüchel and Stepf, para. 2774.]

2767A. From the *trans*-decahydroquinoline (m.p. 45°–45.5° C.) by treatment with methyl iodide and alkali a *trans*-*N*-methyldecahydroquinolone²⁰ is obtained, and this, treated with silver oxide, yields on distillation (76 per cent) a base C₁₁H₂₁N. Hydrogenation of this with platinum or palladium-black catalyst gives *trans*-2-dimethylamino-*n*-propylcyclohexane.

2767B. Similarly from *cis*-decahydroquinoline (b.p. 205° C.) is derived *cis*-2-dimethylamino-*n*-propylcyclohexane. [Fujise, *Ibid.*, 185.]²⁰ Cf. Hydrogenation methylindole, para. 2806.

2768. Quinoline: Hydrogenation with Ipatiev's Technique, with Osmium-ceria Catalysts.²¹ The presence of 1 per cent of osmium dioxide in the cerium oxide-asbestos catalyst causes a more intense hydrogenation of quinoline beyond the tetrahydro-stage which is reached with cerium dioxide alone, thus causing a diminution in the amount of substances of high boiling-point. On the other hand, the use of the combined catalyst (20 or 1 per cent of cerium dioxide with 1 or 20 per cent of osmium dioxide) induces the production of compounds of low boiling-point by further change from decahydroquinoline. From the products of high boiling-point a base, b.p. 275–290°/15 mm., is isolated which, on the basis of analyses and ability to give an additive product with methyl iodide, is regarded as 7-methyl-1 : 2 : 3 : 4 : 7 : 8-hexahydro-1 : 1'-quinolyl. The substance, 1 : 2'-methyl-3'-ethylpiperidino-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroquinoline (dihydrochloride, m.p. 276°), is derived from the fractions of lower boiling-point.

From the products of the interrupted hydrogenation of quinoline the following compounds are isolated: from the fraction of b.p. 150°–175°, the hydrochlorides, C₁₀H₂₀N₂, HCl, m.p. 226°, and C₉H₁₇N, HCl, m.p. 156°, probably derived respectively from 2-amino-3-methyldecahydroquinoline and 2-methyl-3-ethyl-piperidine; from the fraction of b.p. 175°–190°, a hydrochloride, C₁₃H₂₄N₂·2HCl, m.p. 172°, probably derived from 2-amino-3-methyldidecahydro-1 : 1'-quinolyl, a base, C₁₄H₂₆N₂, possibly 1-piperidino-decahydroquinoline, and a ferrocyanide, C₁₄H₂₇N₂·H₄FeC₆N₆, probably a salt of 1-methyl-2 : 3-diethyldecahydroquinoline. Treatment of the fractions of b.p. 175°–190° and 190°–200° in alcohol with carbon dioxide or distillation in a current of carbon dioxide yields the compounds C₁₈H₃₄O₂N₂ and C₂₇H₄₆O₂N₂, respectively.²²

2769. When quinoline is hydrogenated by Ipatiev's method in presence of varying amounts of osmium and cerium dioxides, the properties of the resulting liquid mixtures depend both on the amounts and on the proportions in which the two catalysts are present. With cerium oxide, tetrahydroquinoline is formed almost exclusively. With

²⁰ *Brit. Chem. Abst.*, 1928, 1022A. The intermediate *trans*-methyl compound sometimes is called a quinolone, the corresponding *cis*-compound a quinoline.

²¹ Sadikov and Mikhailov, *Ber.*, 1928, **61B**, 1801.

²² *Brit. Chem. Abst.*, 1928, 1257A.

osmium oxide, higher reduction products, up to decahydroquinoline, together with condensation products of hexahydroquinoline and alkylated derivatives due to the partial decomposition of the ring compounds, are obtained. If both osmium and cerium oxides are present, both condensation of hydrogenated quinoline derivatives and fission of the rings with formation of piperidine compounds, and secondary reactions, resulting in alkylamine derivatives, occur. Complex secondary reactions are especially prominent if the hydrogenation is carried on intermittently. Since the primary products of hydrogenation are very reactive, they must be removed as soon as formed.²³

2769A. Interrupted Hydrogenation of Quinoline with Osmium-ceria.²⁴ Quinoline and the catalyst (asbestos with 20 per cent of osmium dioxide and 1 per cent of cerium dioxide) are placed in an Ipatiev autoclave under 100 atmospheres of hydrogen. The apparatus is placed in an electric furnace pre-heated to 320°–340°, and the times required for the incidence of maximum pressure and subsequently the fall in pressure are observed. The first period is very variable and is followed by an induction period succeeded by one of oscillatory absorption, after which the catalyst becomes exhausted. If, however, the apparatus is cooled to the atmospheric pressure, hydrogenation of the quinoline again proceeds. It appears therefore that the permanent maintenance of high optimal temperatures is not necessary for the hydrogenation of the majority of cyclic compounds and that the high temperature only excites a process which subsequently occurs independently of temperature. Prolonged exposure to a high temperature tends to impair the activity of the catalyst.²⁵

2770. Isoquinoline is reduced only to 1:2:3:4-tetrahydroisoquinoline when hydrogenated in the presence of colloidal platinum under conditions which lead to the decahydrogenation of quinoline. If, however, the concentration of the catalyst is increased, a further absorption of hydrogen occurs steadily, although not very rapidly, and decahydroisoquinoline, b.p. 207° is quantitatively produced. [Skita, *Ber.*, 1924, **57B**, 1977. *J. Chem. Soc. Abst.*, 1924, i, 140.]

2771. Hydrogenated quinoline compound is used as auxiliary in vulcanization.²⁶

2772. Non-catalytic Hydrogenation of Quinolines—by heating the hydriodide with hydriodic acid and red phosphorus. Many derivatives are described. [Yamaguchi, *J. Pharm. Soc., Japan*, 1926, No. **533**, 556; **535**, 749; *Chem. Abst.*, 1927, **21**, 2696.]

2773. Hydrogenation of quinoline hydrogen oxalate with colloidal platinum gives, chiefly, *trans*-decahydroquinoline with 10 per cent of a (liquid) *cis*-isomer. In the presence of hydrochloric acid the *cis*-isomer is formed to the extent of 65 per cent. In neutral solution the tetrahydroquinoline is obtained.²⁷

2774. *cis*-Decahydroquinoline.²⁸ Attempts to prepare 2 ketodecahydroquinoline by the catalytic hydrogenation of *o*-nitrocinnamic acid or its cyclohexyl ester, m.p. 55°–56°, gave principally 2-keto-1:2:3:4-tetrahydroquinoline. Although quinoline had been reduced to the decahydro-derivative in many ways, the formation of more than one isomeride had not hitherto been observed. Hydrogenation of quinoline hydrogen oxalate in presence of colloidal platinum affords, however, in addition to *trans*-decahydroquinoline, m.p. 48°, b.p. 203°/735 mm., a liquid, *cis*-isomeride (10 per cent), b.p. 205°/735 mm. In presence of excess of hydrochloric acid the product contains 65 per cent of this new isomeride, while in neutral solution only 1, 2, 3, 4-tetrahydroquinoline is formed.²⁹

²³ Sadikov and Mikhailov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1557; *Brit. Chem. Abst.*, 1929, 327A.

²⁴ *Idem*, *ibid.*, 1797; *Brit. Chem. Abst.*, 1928A.

²⁵ Sadikov and Mikhailov, *Ber.*, 1928, **61B**, 1797; *Brit. Chem. Abst.*, 1928, 1257A.

²⁶ U. S. Pat. 1,547,555, July 28, 1925, to Bögemann, Imhoff and Schepss (assignors to Farbenfabr. vorm. F. Bayer u. Co.).

²⁷ Lehmstedt, *Ber.*, 1927, **60B**, 1370; *Chem. Abst.*, 1927, **21**, 2903.

²⁸ Hüchel and Stepf, *Ann.*, 1927, **453**, 163.

²⁹ *Brit. Chem. Abst.*, 1927, 572A.

2775. 8-Hydroxyquinoline to decahydro-quinoline (10 per cent), and 2 isomeric 8-hydroxy-decahydroquinolines in 50–60 per cent and 30–40 per cent yield, respectively. Acetic acid solution : 40°–45° C. : platinum-black catalyst. [Fujise, *Sci. Papers Inst. Phys. Chem. Res.*, Tokyo, 1928, **8**, 161.]

2776. 2-Propylquinoline in decahydronaphthalene, with a nickel catalyst hydrogenates at 170° to a mixture 2-propyl-1 : 2 : 3 : 4-tetrahydroquinoline (65 per cent) and 2-propyl-5 : 6 : 7 : 8-tetrahydroquinoline (35 per cent).

2776A. 4-Phenyl-2-methylquinoline gives 4-phenyl-2-methyl-5 : 6 : 7 : 8-tetrahydroquinoline (84 per cent) and 4-phenyl-2-methyl-1 : 2 : 3 : 4-tetrahydroquinoline.

2776B. 2 : 3 : 4-Trimethylquinoline at 155°–160° yields 2 : 3 : 4-trimethyl-5 : 6 : 7 : 8-tetrahydroquinoline with 2 per cent of 2 : 3 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoline.

2776C. 2 : 6-Dimethylquinoline at 105° yields 2 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (98.5 per cent) and 2 : 6-dimethyl-5 : 6 : 7 : 8-tetrahydroquinoline (1.5 per cent).

2776D. 2 : 4 : 5 : 8-tetramethylquinoline at 160°–170° gives 2 : 4 : 5 : 8-tetramethyl-1 : 2 : 3 : 4-tetrahydroquinoline (96 per cent) and 2 : 4 : 5 : 8-tetramethyl-5 : 6 : 7 : 8-tetrahydroquinoline.

2776E. 2 : 4-dimethyl-7 : 8 : 9 : 10-tetrahydro- α -naphthaquinoline hydrogenates with great difficulty to 2 : 4-dimethyl-1 : 2 : 3 : 4 : 7 : 8 : 9 : 10-octahydro- α -naphthaquinoline.

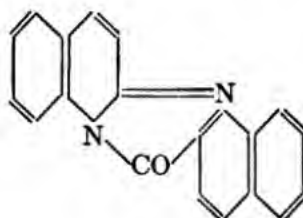
2776F. 2 : 4-methyl- α -naphthaquinoline yields a mixture of 2 : 4-dimethyl : 7 : 8 : 9 : 10-tetrahydro- α -naphthaquinoline and the octahydrobase. [von Braun, Gmelin and Petzold, *Ber.*, 1924, **57B**, 382.]

2777. Preparation of a *Bz*-tetrahydrohydroxyquinoline.³⁰ 6-Hydroxy-2 : 4-dimethylquinoline is treated with molecular hydrogen in the presence of a catalyst containing nickel. For example, hydrogen under pressure is allowed to act on 6-hydroxy-2 : 4-dimethylquinoline dissolved in decahydro-naphthalene at 180°–190° in the presence of nickel. The mixture is diluted with alcohol, filtered, and the solvents distilled off, leaving a crystalline substance insoluble in alkali. 5 : 6 : 7 : 8-Tetrahydro-6-hydroxy-2 : 4-dimethylquinoline, $C_{11}H_{15}ON$, has m.p. 162°, b.p. 181°–183°/15 mm. The O-benzoyl compound, m.p. 199°–200°, made by warming the base in chloroform solution with benzoyl chloride, is an effective anaesthetic.³¹

2778. 8-Methoxy-2-styrylquinoline to 8-methoxy-2- β -phenylethylquinoline. Palladium charcoal catalyst.

2778A. 8-Methoxy-2-*mp*-methylenedioxy-styrylquinoline to 8-methoxy-2-*mp*-methylenedioxyphenylethylquinoline. Palladium charcoal catalyst. [Troger, *et al.*, *J. prakt. Chem.*, 1926, **114**, ii, 199.]

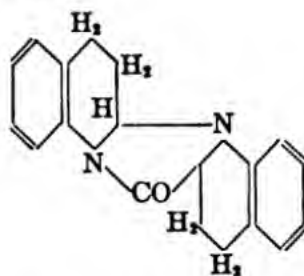
2779. Quinoline red (Besthorn) to $C_{19}H_{15}ON_2$. Very slowly with palladium-black: rapidly with Adams' platinum-black catalyst in absolute alcohol. The red coloring matter appears to be:



³⁰ Ger. Pat. 423,026, Aug. 10, 1923, to J. D. Riedel A.-G.

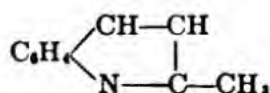
³¹ *Brit. Chem. Abst.*, 1926, 513B.

and its colorless hydrogenation product:



[Wieland, Hettche and Hoshino, *Ber.*, 1928, **61B**, 2376.]

2780. Quinaldine

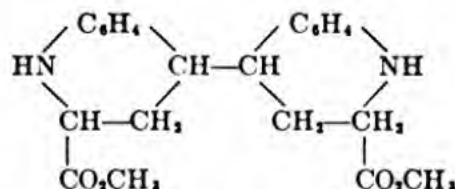


to decahydroquinaldine. Gas phase : 180° : active nickel catalyst. [Sabatier and Murat, *Compt. rend.*, 1914, **158**, 309.]

2780A. γ -Dichloro- α -(2-quinolyl)propene in glacial acetic acid solution with a palladized charcoal gives γ -dichloro- α -(2-quinolyl)propane. [Kondo and Matsuno, *J. Pharm. Soc., Japan*, 1929, **49**, 445; *Chem. Abst.*, 1929, **23**, 4218.]

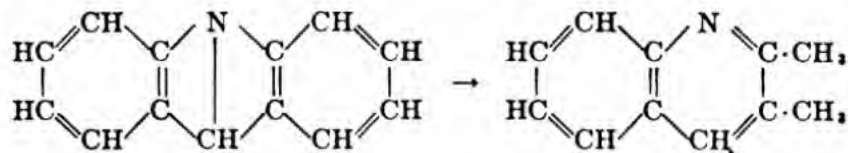
2781. Quinaldine to tetrahydroquinaldine. Suspension in glacial acetic acid 120 cc. : Adams' platinum-black catalyst, 0.3 g. to 10 g. quinaldine : 50°-60° C. [Wieland, Hettche and Hoshino, *Ber.*, 1928, **61B**, 2377.]

2781A. The methyl ester, treated similarly, gives the corresponding tetrahydro ester. If, however, palladium-black catalyst be employed a bi-molecular compound results: γ -ditetrahydroquinolyl- α -dicarboxylic acid dimethyl ester:



[Wieland, Hettche and Hoshino, *Ber.*, 1928, **61B**, 2378.]

2782. Acridine to $\alpha\beta$ -dimethyl-quinoline. Gas phase : 250°-270° : nickel catalyst.



[Padoa and Fabris, *Gazz. chim. ital.*, **38** (I), 233-236, *Lincei*, 1907 **16** (1), 921; *Chem. Centr.*, 1907 (2), 612.]

2783. Ethyl-3 : 6-endomethylene-1 : 2 : 3 : 6-tetrahydro-1 : 2-pyridazine-1 : 2 dicarboxylate in alcoholic solution, with palladium catalyst, is hydrogenated to ethyl-3 : 6-endomethylene-1 : 2-piperidazine-1 : 2 dicarboxylate. [Diels, Blom and Koll, *Ann.*, 1925, **443**, 242.]

2784. 3-Carboxymethyl-6-benzal-2, 5-diketo-piperazine (methyl ester) and its isomer 3-carboxymethylene-6-benzyl-2, 5-diketo-piperazine (methyl ester) on catalytic hydrogenation yield the same 3-carbomethoxymethyl-6-benzyl-2, 5-diketo-piperazine. [Bergmann and Enslin, *Z. physiol. Chem.*, 1928, **174**, 76; *Chem. Abst.*, 1928, **22**, 1757.]

2785. Atophan (2-phenylcinchoninic acid) to tetrahydro-atophan. Glacial acetic acid solution : 50° : $\frac{1}{2}$ to 1 atmosphere excess pressure : colloidal platinum catalyst. (With $\frac{1}{2}$ atmosphere no decahydro-atophan is formed.) Ultimate product of hydrogenation is perhydroatophan.

2785A. 2-Phenyl-quinoline to 2-phenyl-1 : 2 : 3 : 4-tetra-hydroquinoline. 2 atmospheres. [Skita, *et al.*, *Ber.*, 1926, **59**, 2683.]

2786. Humulon ($C_{21}H_{30}O_6$, from hop resin) on catalytic hydrogenation yields β -methylbutane and a compound, $C_{16}H_{24}O_6$, which is probably a substituted quinol. [Wieland, with Schneider and Martz, *Ber.*, 1925, **58B**, 102.]

2787. Anhydrolupinine (or its salts) to "lupinane" (probably $C_9H_{16}NCH_3$). Acetic acid solution, platinum-black catalyst.³²

2788. Hydrogenation of Glyoxaline Ring.³³ Hydrogenation of lophine (2 : 4 : 5-triphenylglyoxaline) 1.028 g., in acetic acid 30 cc., with 0.758 platinum-black catalyst gives 2 : 4 : 5-tricyclohexyl-4 : 5-dihydroglyoxaline. Accelerated by a few milligrams of hydrolophine. Fourteen hours shaking : catalyst reactivated three times by shaking with air.

2788A. Amarine (2 : 4 : 5-triphenyl-4 : 5-dihydroglyoxaline) on hydrogenation gives a mixture of the above 2 : 4 : 5-tricyclohexyl-4 : 5-dihydroglyoxaline and 2 : 4 : 5-tricyclohexyltetrahydroglyoxaline.

2788B. Hydrogenation failed in the cases of : glyoxaline, 2 : 4 : 5-trimethylglyoxaline, 2-methyl-4 : 5-dihydroglyoxaline, histidine, and benziminazole.

2789. 3-Benzal-pyrimidazolon-2 to 3-benzyl-pyrimidazolon. Hydrochloride in suspension in absolute ethanol : platinum-sponge catalyst. [Reindel and v. Putzer-Reyegg, *Ber.*, 1926, **59B**, 2929.]

2790. Antipyrine to dihydroantipyrine. Aqueous solution : 5 per cent platinum-black : hydrogen pressure 1.08 atmospheres. Hydrogenation slow.

2790A. Nitroantipyrine to acetylamino-antipyrine. Glacial acetic acid solution : 7 per cent platinum-black : hydrogen pressure 1-2 atmospheres. [Waser, *Helv. Chim. Acta*, 1925, **8**, 117.]

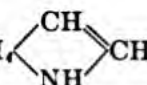
³² Ger. Pat. 396,508, 1922; *J.S.C.I.*, 1924, 891B.

³³ Waser and Gratsos, *Helv. Chim. Acta*, 1928, **11**, 944. Glyoxaline is: $\begin{array}{c} \text{CH}-\text{NH} \\ || \\ \text{CH}-\text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{CH}$ it is the parent substance of iminazoles.

CHAPTER XXVIII

HYDROGENATION OF HETEROCYCLIC COMPOUNDS

II

2800. Indole. Indole, C_8H_7 , over nickel at 200°, takes up 3H₂ and splits into orthotoluidine and methane. [Carrasco and Padoa, *Lincei*, 1906, **14** (2), 699; *Chem. Centr.*, 1906 (2), 683.]

2801. In glacial acetic acid solution, with a platinum-black catalyst, indole is hydrogenated to octahydro-indole (b.p. 182°) and a little dihydro-indole. [Willstätter and Jacquet, *Ber.*, 1918, **51**, 767.]

2802. Indole to perhydroindole (octahydroindole). Platinum catalyst at room temperature.

2803. Indole to *o*-ethyl-hexahydroaniline. 225° : nickel catalyst. The product is not perhydroindole as before believed (cf. von Braun, Bayer and Blessing, *Ann.*, 1924 (i), 545; Willstätter, Seitz and von Braun, *Ber.*, 1925, **58** (B), 385.)

2804. For catalytic hydrogenation of indole bases, with and without opening of the ring, see von Braun and Bayer, *Ber.*, 1925, **58** (B), 387.]

2805. Indole, hydrogenated under pressure at 225° with a nickel catalyst gives 8 per cent unchanged indole, 66 per cent basic substances and a residue of degradation products and ammonia. The basic products are perhydroindole (octahydroindole) and *o*-ethylaniline. By partial hydrogenation at 180° 2 : 3-di-hydroindole is obtained.

2805A. 2-Methylindole at 220° gives a mixture of 2-methyloctahydroindole and 2-methyl-4 : 5 : 6 : 7-tetrahydroindole.

2805B. 3-Methylindole yields 3-methyl-4 : 5 : 6 : 7-tetrahydroindole and 3-methyloctahydroindole.

2805C. 1 : 2-Dimethylindole at 200° gives 1 : 2-dimethyl-4 : 5 : 6 : 7-tetrahydroindole and 1 : 2-dimethyloctahydroindole.

2805D. 2 : 5-Dimethylindole at 250° gives *o*-propyl-*p*-toluidine as the chief product, with some 2 : 5-dimethyloctahydroindole.

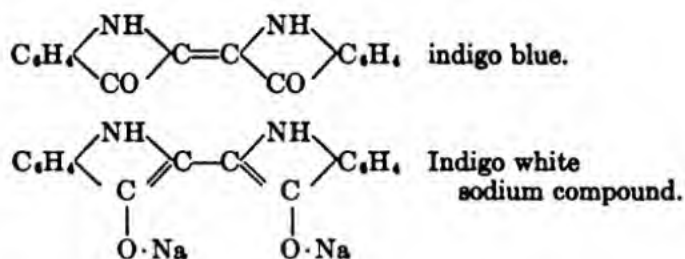
2805E. 2 : 4 : 7-Trimethylindole gives 2-propyl-3 : 6-dimethylaniline. [von Braun, Bayer and Blessing, *Ber.*, 1924, **57B**, 1924, **57B**, 392.]

2806. 2-Methylindole to *cis*-2-methyl-octahydroindole. Glacial acetic acid solution : 40°-45° C. : platinum-black catalyst. By exhaustive methylation this product yields a base *o*-dimethylaminopropenylcyclohexane, and this on catalytic hydrogenation gives *cis*-2-dimethylamino-*n*-propylcyclohexane. [Cf. Hydrogenation of decahydroquinoline, para. 2767B; Fujise, *Sci. Papers Inst. Phys. Chem. Res.*, Tokyo, 1928, **9**, 91.]

2806A. Hadano and Matsuno (*J. Pharm. Soc.*, Japan, 1924, **48**, 904; *Chem. Abst.*, 1929, **23**, 1635) obtained, as main product, *bz*-tetrahydro-2-methylindole, the octahydro derivative being a by-product.

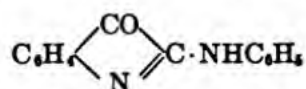
2807. Indigo, suspended in dilute sodium hydrate solution, is reduced to indigo white, in the presence of nickel, at 70°. The same is true of thio-indigo. [Brochet, *Compt. rend.*, 1915, **160**, 306.]

2807A. Note the molecular transformation:



2808. Isatin to dioxyindole. 4-Nitroisatin to 4-aminodioxindole. 4-Nitroisatin-phenylhydroxylamine to 4-aminoisatinanil.

2808A. Isatinphenylhydroxylamine to lactim form of isatin- α -anil,



Nickel catalyst. [Rupe and Apothoker, *Helv. Chim. Acta*, 1926, 9, 1049; *Chem. Abst.*, 1927, 21, 912.]

2809. Isatin and 5-methylisatin gave diisatide and 5, 5-dimethylisatide, respectively, on catalytic reduction. [Wahl and Faivret, *Compt. rend.*, 1925, 181, 790.]

2810. 1-Phenylindole to 2-phenyldihydroindole. Alcohol solution: palladized charcoal catalyst. [v. Braun and Manz, *Ber.*, 1929, 62B, 1059.]

2810A. Diphenylindone to a mixture of 2, 3-diphenyl-1-hydroxydihydroindene and 2, 3-diphenyl-1-ketodihydroindone. Palladium-barium sulphate catalyst. [Schlenck and Bergmann, *Ann.*, 1928, 463, 98-227; *Chem. Abst.*, 1928, 22, 4497.]

2811. 2-Carbethoxy-3-[β , β -dicarbethoxyvinyl] indole to 2 carbethoxy-3-[β , β -dicarbethoxyethyl] indole. Palladium catalyst. [Maurer and Moser, *Z. physiol. Chem.*, 1926, 161, 131.]

2812. Hydroxymethylenehydrindone to hydrindolymethyl alcohol. [Rupe and Wieland, *Helv. Chim. Acta*, 1926, 9, 1001; *Chem. Abst.*, 1927, 21, 582.]

2812A. 2-Cinnamylidene-1-hydrindone to phenylpropylhydrindone. Palladium-charcoal catalyst. [v. Braun and Manz, *Ann.*, 1929, 468, 258; *Brit. Chem. Abst.*, 1929, 561A.]

2812B. 2-Benzylidene-5-methyl-1-hydrindone to benzylmethylhydrindone. [v. Braun, Manz, and Reinsch. *Ann.*, 1929, 468, 277; *Brit. Chem. Abst.*, 1929, 562A.]

2813. Reduction of Vat Dyes to Leuco-compounds. A suspension of the dye in a dry organic solvent is treated with hydrogen in presence of catalysts, such as nickel, cobalt, iron, copper, either alone or mixed with their lower oxides. Thus, a suspension of indigo in dimethylaniline, containing nickel precipitated on kieselguhr, is treated with hydrogen at 90°-100° C. The resulting suspension of leuco-indigo is suitable for conversion into esters.¹

2814. Leuco-compounds of vat dyes are obtained by treating the dyes with hydrogen in the presence of a catalyst, such as nickel. The process may be effected by suspending the dye in water with the addition of an alkali and the catalyst, and introducing hydrogen, or a gas containing hydrogen, while violently agitating the mixture; inorganic salts, such as chlorides or sulphites, may be added, and the reaction mixture may be heated or the process conducted under pressure. An example is given of the production of

¹ *Brit. Chem. Abst.*, 1926, 868B.; French Pat. 601,632, Nov. 6, 1924, to Comp. Nat. mat. col. et manuf. de prod. chim. du nord réunies, Etabl. Kuhlmann; *Brit. Pat.* 271,569, Feb. 26, 1926, to Marschalk.

indigo-white; algol, ciba, helindrone, hydrone, anthracene dyes are also reported as suitable.²

ALKALOIDS

2815. Metanicotine to dihydrometanicotine. 14 g. alkaloid in 100 cc. alcohol and 14.4 cc. concentrated hydrochloric acid : Adams' platinum-black catalyst : one hour. [La Forge, *J. Am. Chem. Soc.*, 1928, **50**, 2483.]

2816. Quinine to dihydroquinine, $C_{20}H_{21}O_2N_3$. Solution in dilute sulphuric acid : platinum-black catalyst : the end of the hydrogenation is reached when the solution does not decolorize potassium permanganate solution.³

2817. In the presence of spongy or colloidal platinum formic acid is decomposed, yielding nascent hydrogen. If this takes place in solutions containing quinine the alkaloid is hydrogenated to hydroquinine.⁴

2818. Cinchonidine to dihydrocinchonidine (m.p. 229°). 7 per cent in hydrochloric acid solution : 1 atmosphere plus pressure : colloidal palladium catalyst. [Skita and Nord, *Ber.*, 1912, **45**, 3316.]

2819. Cinchonine to cinchotine. Liquid phase : colloidal palladium catalyst.⁵

2819A. With colloidal platinum prepared with gum arabic and under a pressure of 2-3 atmospheres, cinchonine in acetic acid solution can be hydrogenated to hexahydrocinchonine. [Skita and Brunner, *Ber.*, 1916, **49**, 1597.]⁶

2820. Quinidine to dihydroquinidine, m.p. 165°. Diluted hydrochloric acid solution : colloidal palladium catalyst : 1 atmosphere plus pressure. [Skita and Nord, *Ber.*, 1912, **45**, 3316.]

2821. Hydrogenated Cinchona Alkaloids. Cinchona alkaloids such as quinine or cinchonidine or their substitution derivatives can be hydrogenated to hexahydro-derivatives by means of hydrogen in the presence of nickel or other catalyst of this group at temperatures above 30° C., and preferably at 60°-80° C. The parent material may be the non-hydrogenated or the dihydro-derivative of the alkaloid in the form of base or salt and may be used dissolved in water, alcohol, or other solvent. For example, a solution of 5 parts of quinine in 100 parts of absolute alcohol is agitated at 20° C. with 3-4 parts of a nickel catalyst in an atmosphere of hydrogen under a pressure of 20-40 lb. per sq. in. The absorption of gas ceases when the quantity of hydrogen corresponding to the production of dihydroquinine has been taken up. On raising the temperature above 40°, absorption (slower) again sets in and at about 80° double the amount of hydrogen absorbed at the first stage will have been taken up. The hexahydroquinine is isolated by evaporating the filtered solution.⁷

2822. Anhydrolupinine to a mixture of inactive α - and β -lupinanes. Palladium-calcium carbonate catalyst.

2822A. Desoxycinchonine or cinchene, to dihydrodesoxycinchonine.

2822B. α -des-*N*-methylsparteine to a dihydro derivative. [Schopf, Thomä, Schmidt and Braun, *Ann.*, **465**, 1928, 97-146.]

2823. Methyl-lupinine to dihydromethyl-lupinine. Dihyrodimethyl-lupinine to tetrahydrodimethyl-lupinine. [Karrer, Canal, Zohner, and Widmer, *Helv. Chim. Acta*, 1928, **11**, 1062; *Brit. Chem. Abst.*, 1929, 200A.]

2824. Morphine to dihydromorphine. Solution in dilute sulphuric acid : platinum-black catalyst.⁸

² *Chem. Abst.*, 1916 **10**, 696; U. S. Pat. 1,247, 927, Nov. 27, 1927, to Brochet; *Brit. Pat.* 19,848, Sept. 16, 1914.

³ *Brit. Pat.* 3948, 1912, to Verein. Chininfabr. Zimmer & Co.; U. S. Pat. 989,664.

⁴ *Ger. Pat.* 267,306, 1914, to Verein. Chininfabr. Zimmer & Co., *Chem. Centr.*, 1914 (1), 88.

⁵ Paal, *Ger. Pat.* 223,413.

⁶ See also: Freund and Bredenberg *Chem. Zeit.*, 1915, **39**, 109; *J.S.C.I.*, 1915, **34**, 7, 376.

⁷ *Brit. Pat.* to Howards & Sons, Ltd., and Blagden, 250,380, Mar. 24, 1925. U. S. Pat. 1,720,462, July 9, 1929.

⁸ *German Pat.* 260,233.

2825. Diacetyl-morphine (heroin) in hydrochloric acid solution with colloidal platinum catalyst, gives dihydro compound. [Skita and Meyer, *Ber.*, 1912, **45**, 3579.]

With colloidal platinum catalyst also diacetyl-morphine takes up H_2 . [Skita and Brunner, *Ber.*, 1916, **49**, 1597.]

2826. Hydrogenation of organic substances (specifically alkaloids) *in solution* in presence of a nickel catalyst is claimed as the novel feature of U. S. Pat. 1,239,867, Sept. 11, 1917, to Blagden (assignor to Boehringer und Söhne).

2827. Preparation of Hydrogenated Alkaloids.⁹ Alkaloids or their salts can be smoothly hydrogenated in aqueous solution or suspension by means of molecular hydrogen in the presence of nickel suboxide; the temperature may be normal or somewhat above (up to 60 ° C.), and the pressure normal or slightly raised. Thus, hydroquinine and dihydromorphine are prepared from quinine hydrochloride and morphine, respectively, while cinchonine gives hydrocinchonine, an oily liquid which is decomposed by heat. [*J. Chem. Soc.*, 1918, **113** and **114**, 546.]

2828. In the production of dihydromorphine, hydrogen is allowed to act upon acid, neutral, aqueous, or water-alcohol opium extracts, in the presence of a catalyzer; the acidified solution is evaporated, and the residue is treated with absolute alcohol, the dihydromorphine salt remaining undissolved.¹⁰ [*Chem. Abst.*, 1915, **9**, 955.]

2829. Organic compounds of the opium group are hydrogenated with formic acid and a finely divided metal of the platinum group or a colloidal solution of such metal. Thus, hydromorphine and hydrocodeine are prepared with the aid of palladium-black as the catalyst.¹¹

2830. Benzyl ethers of phenols are converted into phenols by treatment with hydrogen in the presence of noble metals as catalysts. For example, an aqueous suspension of benzylmorphine hydrochloride is shaken with hydrogen in the presence of palladium-impregnated charcoal, 2 molecules of hydrogen being absorbed. The solution is filtered, made alkaline, extracted with ether to separate toluene, and treated with ammonium carbonate to precipitate dihydromorphine. The process is of value in the synthesis of phenols where temporary protection of the hydroxyl group by benzylation is necessary.¹²

2831. Morphine Group. For a large number catalytic hydrogenations in this group see: Cahn, *J. Chem. Soc.*, 1926, 2562-2573, and references there given. Also Braun and Cahn, *Annalen*, 1926, **451**, 55; *Brit. Chem. Abst.*, 1927, 266A.

2832. Codeine to dihydrocodeine. Liquid phase: in dilute sulphuric acid: platinum-black catalyst: pressure more than 1 atmosphere.¹³

2833. Bromocodeine 10 per cent acetic acid solution with palladium-charcoal catalyst quickly forms bromo-dihydrocodeine; the hydrogenation continues, yielding, after several hours, dihydrocodeine. Chlorocodeine gives only monochlorodihydrocodeine. [Speyer and Rosenfeld, *Ber.*, 1925, **58B**, 1110.]

2834. Bromocodeinone to dihydrocodeinone. Acetic acid solution: palladium on charcoal catalyst.

2835. Dihydrodeoxycodine to β -tetrahydrodeoxy codeine. Colloidal palladium catalyst. [Speyer and Sarre, *Ber.*, 1924, **57(B)**, 1404.]

2836. Hydroxycodine-hydrazone to hydroxydihydro-codeinone-ketimine and ammonia. Acetic acid solution: palladium catalyst. In aqueous acetone solution only $1H_2$ is taken up with the formation of hydroxydihydrocodeinone-dimethylketazine. [*Ibid.*, 1422.]

2837. Bromohydroxycodine to hydroxydihydrocodeine. Palladium catalyst.

2838. Dibromohydroxycodine to hydroxydihydrocodeinone. Palladium catalyst.

2839. In bromohydroxydihydrocodeinone on treatment with double normal sodium hydroxide yields what is regarded as bromo-7, 8, 14-trihydroxydihydrocodeinone, and

⁹ C. F. Boehringer & Söhne, Ger. Pat. 306,939; *Chem. Zentr.*, 1918, ii, 421.

¹⁰ Ger. Pat. 278,107, May 27, 1913. F. Hoffmann La Roche & Co.

¹¹ *Chem. Abst.*, 1915, **9**, 126; *Brit. Pat.* 14,247, June 19, 1913, to Verein. Chininfab. Zimmer.

¹² Ger. Pat. 407,487, Nov. 27, 1923, to Merck (assignees of Wolfes and Krause).

¹³ Ger. Pat. 260,233.

this, on hydrogenation (dehalogenation) with a palladium catalyst, gives 7, 8, 14-trihydroxydihydrocodeinone. [*Ibid.*, 1409-1422; *J. Chem. Soc.*, 1924 (i), 1229.]

2840. Hydroxycodeinone hydrazone ($C_{18}H_{21}O_4N_2$) to a base $C_{18}H_{21}O_4N_2$ (very unstable) and ammonia. Acetic acid solution: palladium catalyst. In acetone solution, not only is the 8, 14-double bond saturated but the acetone reacts with the production of a ketazine.

2841. The hydrazone with palladium-charcoal gives dihydrohydroxycodeinone ketimine. With acetone solvent and colloidal palladium catalyst is formed dihydroxycodeinone-dimethyl ketazine. [Speyer and Sarre, *Ber.*, 1924, 57B, 1422.]

2842. Neopine to Dihydrocodeine. A solution of neopine (2.5 g.) in water (25 cc.) and acetic acid (1 cc.) containing colloidal palladium (5 cc. of 0.5 per cent palladous chloride) was stirred in hydrogen, when the palladium was at once flocculated. More palladous chloride solution (10 cc.) was added, but flocculation again occurred. In about fifteen hours, 180 cc. of hydrogen were absorbed (equivalent to 176 cc. at N. T. P.) [van Duin, Robinson and Smith, *J. Chem. Soc.*, 1926, 907.]

2843. Ozodihydrocodeine (obtained by ozonization of dihydrocodeine dissolved in formic acid), when hydrogenated in neutral solution with a palladium catalyst, takes up hydrogen at the lactone ring (which, of course, splits), forming deoxydihydro-morphinic acid.

2844. Ethyl dihydromorphine is hydrogenated to ethyl-deoxydihydro-morphinate. [Speyer and Popp, *Ber.*, 1926, 59B, 390.]

2845. Anhydrolaudalinenitroacetylaminomethoxytoluene to anhydrolaudaline-2-amino-4-acetyl-amino-3-methoxytoluene. Nitro-base 2 g., acetic acid 50 cc., palladous chloride (2 per cent solution in acetic acid) 10 cc.: agitated with hydrogen three hours. [Robinson and Shinoda, *J. Chem. Soc.*, 1926, 129, 1993.]

2846. Methylenepapaverine to dihydromethylene-papaverine. Dissolved in 10 per cent acetic acid: Palladium charcoal catalyst. [Späth and Polgar, *Ber.*, 1926, 59, 2790.]

2847. Thebaine hydrochloride hydrogenated in the presence of (initial) palladous chloride and gum arabic gives a 50-60 per cent yield of dihydrothebaine.

2848. De-*N*-methyldihydrothebaine hydrogenated in presence of acid palladous chloride yields dihydrode-*N*-methyldihydrothebaine. Reduced in acetic acid by Skita's method the de-*N*-methyldihydrothebaine gives the ketone dihydrode-*N*-methyldihydrothebainone.

2849. $C_{18}H_{20}O_3$, produced by treatment of the methiodide of dihydrode-*N*-methyldihydrothebaine with silver oxide and distillation, yields on hydrogenation in alcohol solution in presence of palladium-black, a phenol $C_{17}H_{22}O_3$. [Wieland and Kotake, *Ann.*, 1925, 444, 69.]

2850. Hydrogenation of thebaine, in presence of platinum-black catalyst, and in a solvent perfectly acid-free, gave an oily phenolic product, yielding 80 per cent of dihydrothebainone on warming with 2N-HCl.

2850A. The nitrogen-free ether obtained by the Hofmann degradation of dihydrode-*N*-methyl-dihydrothebaine gave, on hydrogenation in alcoholic solution with palladium-black catalyst, the ketophenol. On repeating the operation in alcohol freed from every trace of acid, by the addition of very little sodium bicarbonate, the intermediate thebaine derivative was obtained. [Wieland and Munio Kotake, *Ber.*, 1925, 58B, 2009.]

2851. Thebaine: Catalytic Hydrogenation of Enol Ethers. Thebaine and its nitrogen free degradation product take up only 2 molecules of hydrogen. The resulting dihydro-derivatives, like thebaine itself, are converted in the same way as an enol ether, into a ketone by loss of CH_3OH . A study of the catalytic hydrogenation of enol ethers, open and cyclic, showed that they are readily hydrogenated in conditions under which thebaine and its derivatives are unaffected.

2851A. 1-Methoxy-1-cyclohexene in ethyl ether solution with palladium-black (0.3 g. catalyst to 2.3 g. of the enol ether) is hydrogenated to hexahydroanisole. [Wieland and Garbech, *Ber.*, 1926, 59B, 2490. Cf. Schöpf, *Ann.*, 1927, 452, 211; *Chem. Abst.* 1927, 21, 2697.]

2852. Methylthebainonemethine to a dihydro compound. Colloidal palladium catalyst. This product, treated with sodium amalgam and alcohol, is reduced to dihydrothebainolmethine. This last compound is also obtained by catalytic reduction of methylthebainol methine.

2853. Thebainonemethine treated with sodium amalgam gives thebainolmethine, which, in 10 per cent acetic acid, is hydrogenated catalytically to dihydrothebainol methine. [Schöpf and Borkowsky, *Ann.*, 1927, **458**, 148.]

2854. α -Thebaizone (ozonolysis product of thebaine) to (a phenolic) dihydrothebaizone. Methanol solution: platinum oxide solution.

2855. Deoxythebaizone (from α -thebaizone by reduction with aluminum amalgam in moist ether) after hydrolysis with *N*-hydrochloric acid, is catalytically hydrogenated to dihydrodeoxythebaizonic acid.

2856. Isodihydrothebaizonic acid (ozonolysis product of dihydrothebaine in acid solution) to the tetrahydro acid with isodihydrothebaizone. [Wiand and Small, *Ann.*, 1928, **467**, 17; *Brit. Chem. Abst.*, 1929, 81A.]

2857. Norcyanthebenine (produced from thebaine by action of bromocyanogen) on hydrogenation absorbs 4 molecules of hydrogen to form an oily base which, with methyl iodide, gives $C_{10}H_{16}O_2NI$. [Speyer and Rosenfeld, *Ber.*, 1925, **58**, 1125.]

2858. Vinylphenanthrene (exhaustive methylation product of laurotetanine) to tetramethoxy-8-ethylphenanthrene (identical with product synthesized from 3:4-dimethoxyethyl benzene). Palladium colloidal catalyst (from the chloride in gum arabic protective.) [Barger and Silberschmidt, *J. Chem. Soc.*, 1928, 2919; *Brit. Chem. Abst.*, 1929, 80A.]

2859. Strychnine. Dissolved in 50 per cent acetic acid and hydrogenated in presence of a palladium-norite catalyst, strychnine, after three to four hours, gives a 93 per cent yield of dihydrostrychnine. No further hydrogenation takes place on raising the temperature to 100° C.

2860. Isostrychnine also gives a dihydro derivative, dihydroisostrychnine, on catalytic reduction.

2861. Strychnidine gives dihydrostrychnidine. [Oxford, Perkin and Robinson, *J. Chem. Soc.*, 1927, 2389.]

2861A. Vomisine, $C_{11}H_{14}O_4N_2$ (a new alkaloid of *strychnos*) in dilute acetic acid solution with platinum oxide catalyst and hydrogen yields dihydrovomisine. The bromo compound gives bromodihydrovomisine. [Wiand and Oertel, *Ann.*, 1929, **469**, 193; *Brit. Chem. Abst.*, 1929, 708A.]

2862. Brucine to dihydrobrucine. Liquid phase, solution in nitric acid: 2 atmospheres: colloidal palladium catalyst.¹⁴

2863. Dehydrosparteine, $C_{15}H_{24}N_2$ (oxidation product of sparteine), to ψ -sparteine. Platinum-black catalyst. [Wolfenstein and Reitmann, *Biochem. Z.* 1927, **186**, 269; *Brit. Chem. Abst.*, 1927, 887A.]

2864. Methylsparteine. A mixture of α - and β -methylsparteine could not be catalytically hydrogenated. But the mono-hydroiodide of α -methylsparteine, in glacial acetic acid solution with a platinum oxide catalyst, was hydrogenated to dihydro- α -methylsparteine. [Winterfield, *Arch. Pharm.*, 1928, **266**, 299.]

2865. Oxyserolene to hydro-oxyserolene. Colloidal palladium catalyst. [Polonovski and Polonovski: Constitution of Eserine, etc. *Bull. Soc. Chim.*, 1925 (iv), **37**, 744.]

2866. Colchicine to tetrahydrocolchicine. Liquid phase: colloidal palladium catalyst: 2 atmospheres pressure.¹⁵

¹⁴ Skita and Paal, Ger. Pat. 230,724, *Chem. Zentr.*, 1911 (1), 522.

¹⁵ Hoffmann, La Roche & Co., Ger. Pat. 279,999, *Chem. Zentr.*, 1914 (2), 1214.

CHAPTER XXIX

DEHALOGENATION

2900. Removal and Determination of Halogens in Organic Compounds by Catalytic Reduction. Organic halogen compounds shaken with water (or alcohol) in the presence of palladium-calcium carbonate catalyst and of alcoholic potash in a current of pure hydrogen are quantitatively dehalogenized, with absorption of hydrogen. The halogen taken up by the alkali can be estimated in the usual way. [Busch and Stove, *Ber.*, 1916, **49**, 1063; *Chem. Abst.*, 1916, **10**, 2727.]

2900A. The catalyst is made by shaking an aqueous suspension of freshly precipitated calcium carbonate with palladium chloride. It is easily poisoned. Benzene, chloroform, acetone and especially carbon disulphide cannot be used as solvents: compounds containing phosphorus, sulphur or arsenic cannot be dealt with.

2900B. Benzylidene chloride and benzotrichloride are completely dechlorinated by this method, but dichloromethylmethylhexadienones are resistant. [*Ibid.*, *J. Chem. Soc., Abst.*, 1916, ii, 534.]

2901. Kelber¹ notes that palladium has been used for the displacement of halogens from organic compounds, and it has been found that the reaction in presence of palladinized calcium carbonate proceeds so completely that the hydrogenation process may be used as a quantitative method for the determination of halogens.

2901A. Equally satisfactory results may be obtained with nickel catalysts and in this case it is not necessary to recover the catalyst. A special shaking tube has been designed for the use of this method for analytical purposes. This vessel is easily filled with the catalyst and the halogen derivative can be added subsequently; any contact of the liquid and catalyst with rubber connections is avoided and the product of the reaction can be quantitatively removed. The catalyst is prepared by heating basic nickel carbonate in a current of hydrogen at 310° to 320° C., cooling, and passing a current of carbon dioxide over the material. The catalyst may be kept for a long time in closed vessels. For each determination, 3 g. of the catalyst is placed in the reaction tube, shaken with water or dilute alcohol, and 0.5 to 1.0 g. of alkali hydroxide in presence of hydrogen until no more of the gas is absorbed, and the substance to be analyzed is then sucked in and the funnel rinsed. Shaking is continued for some time after the reaction with the hydrogen is complete, the nickel is filtered off and washed, and the halogen in the liquid determined either gravimetrically or by titration. In the case of amino compounds or compounds which form precipitates with silver, the organic by-products should be shaken out with ether before making the halogen determination.

2901B. ter Meulen. Improvements in the hydrogenation method for organic chemical analysis. [*Chem. Weekblad.*, 1926, **23**, 348.]

2901C. Yakugakuzasshi. Catalytic reductions in quantitative analysis: bibliography. [*J. Pharm. Soc., Japan*, 1928, No. **506**, 282.] Explanatory bibliography of some 200 references to the use of catalytic reductions with palladium and platinum.

2902. Dehalogenation of Organic Compounds. Rosenmund and Zetzsche² find that both colloidal palladium protected by gum arabic, and palladinized barium sulphate are

¹ *Ber.*, 1917, 305; *J.S.C.I.*, 1917, 568 and 1916, 382 and 1130.

² *Ber.*, 1918, **51**, 578.

efficient catalysts for dehalogenation and that it is usually advisable to have an alkali present to neutralize the halogen hydracid as it is formed. Many substances react even if merely suspended in aqueous alkalis. In the case of halogen derivatives of ethylenic compounds, the halogen may sometimes be removed without saturating the double linking or the halogen derivative of the saturated compound may be formed. Frequently the reaction proceeds smoothly to hydrogenation and removal of halogen. In the case of dihalogen compounds, it is apparently impossible to obtain mono-derivatives.

2902A. The following reductions have been carried out: bromobenzene to benzene; *o*-bromobenzoic acid to benzoic acid; 1:4-bromonitrobenzene to aniline; chlorocaffeine to caffeine; chlorocrotonic acid to crotonic acid; *o*-chlorocinnamic acid to β -phenylpropionic acid; dibromosuccinic acid to succinic acid.²

2903. Reduction of Acid Chlorides by Hydrogenation under Reduced Pressure. Grignard and Mingasson⁴ have successfully used hydrogenation under reduced pressure for the reduction of acid chlorides, an operation that at atmospheric and higher pressures is delicate and beset with difficulties. At 300° C., under 50–300 mm. pressure with a nickel catalyst, benzoyl chloride gives 60 per cent benzaldehyde, with benzoic acid. At 250° C. little benzaldehyde, much toluene and benzoic acid are produced.

2904. For reduction of organic halogen compounds, see a series of articles by Brand (with others) in *J. prakt. Chem.*, 1926 and 1927, e.g., reduction of $\beta\beta\gamma\gamma$ -tetrachloro- $\alpha\alpha\delta\delta$ tetra-*p*-tolylbutane. *J. prakt. Chem.*, 1927, 115 (ii), 335; catalytic reduction of $\alpha\alpha\alpha$ -trichloro- $\beta\beta$ -diarylethanes. *Ibid.*, 351.

2905. Purification of Xylene for Use as Solvent for Catalytic Reduction.⁴ In the catalytic reduction of acid chlorides in toluene or xylene solution, the preliminary method of treatment of the solvent has a large effect on the yield of aldehyde obtained. By preliminary treatment of xylene with phosphoryl chloride or phosphorus pentachloride, under certain prescribed conditions, the yield of aldehyde (from benzoyl chloride) was considerably reduced, and in one case (boiling the xylene with phosphoryl chloride for one and one-half hours, followed by distillation) almost to zero, with an accompanying increase in the yields of ester and non-volatile hydrocarbon products. The effects of other purifying reagents was investigated, and treatment with either aluminum chloride or concentrated sulphuric acid was found to produce a solvent in which very little or no formation of aldehyde occurred, the products being mainly hydrocarbons.⁵

2906. Various Solvents for the Catalytic Synthesis of Aldehydes from Acid Chlorides.⁷ The utility of a large number of substances as solvents in the catalytic reduction of benzoyl chloride, first in the commercial state at their boiling-point, then after purification, and finally with the addition of a regulator (quinoline-*s*) has been investigated. Decalin and tetralin, which, having themselves been prepared by catalytic reduction, are free from catalyst poisons, give good yields of benzaldehyde in their crude state, and after purification and with the addition of a small quantity of a regulator give, respectively, 86 per cent and 82 per cent yields after two hours at 180°. The maximal yield obtained with anisole as a solvent is 84 per cent, while with redistilled turpentine in the presence of a regulator, a 92 per cent yield of benzaldehyde is obtained in one and three-quarter hours.

2907. Solvents which are themselves reduced and can interact with the benzoyl chloride have also been investigated. Thus with amyl and hexalin acetates the corresponding benzoates are obtained; with phenetole, phenyl benzoate; and with acetic anhydride, benzoic anhydride, this reaction providing a ready method for the prep-

² *J. Chem. Soc.*, 1918, 113 and 114, Abs. I, 339. See also: Borsche and Heimbürger, *Ber.*, 1915, 48, 452; *Chem. Abst.*, 1915, 9, 1773.

⁴ *Compt. rend.*, 1927, 185, 1173; *Chem. Abst.*, 1928, 22, 1766.

⁵ Zetzsche and Arndt, *Helv. Chim. Acta*, 1926, 9, 173–177. *Ibid.*, 1925, 8, 591.

⁶ *Brit. Chem. Abst.*, 1926, 405A.

⁷ Zetzsche, Enderlin, Flütsch and Menzi, *Helv. Chim. Acta*, 1926, 9, 177–181.

aration of acid anhydrides from acid chlorides. In *s*-tetrachloroethane solution, the products are benzaldehyde (17 per cent) and benzyl benzoate (70 per cent), while with nitrobenzene as solvent are obtained the aldehyde and ester, benzanilide and benzoyldiphenylamine, the relative proportions varying with the proportions of benzoyl chloride and nitrobenzene in the original mixture.⁸

2908. Aldehydes from Acid Chlorides.⁹ One of the best methods for the preparation of aldehydes consists in the hydrogenation of the acid chlorides in boiling xylene or cumene with palladinized barium sulphate (5 per cent of metal) or nickel as the catalyst.¹⁰ *p*-Methylcarbonatobenzaldehyde, $\text{CH}_3\text{O}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$, thus may be prepared in 95 per cent yield.¹¹

2909. Stearyl chloride to stearic aldehyde. In a hydrocarbon (cumene) solution: palladium-black catalyst, precipitated on barium sulphate. [Rosenmund, *Ber.*, 191, 585.] The barium sulphate should be freshly precipitated. A dimeride ($\text{C}_{18}\text{H}_{34}\text{O}_2$) is also formed, which does not give aldehyde reactions, but yields stearylaldehyde on distillation at 140° – 200° C. under 1 mm. Hg. [Feulgen and Behrens, *Z. physiol. Chem.*, 1928, 177, 221.]

2910. Butyryl chloride to butyl aldehyde. Liquid phase (solution in a hydrocarbon): palladium on barium sulphate catalyst. [Rosenmund, *Ber.*, 1918, 51, 585.]

2911. Benzoyl chloride to benzaldehyde (97 per cent). Liquid phase: palladium-black catalyst, precipitated on barium sulphate or Kelber's nickel catalyst. The substrate is dissolved in xylene or cumene. [Rosenmund, *Ber.*, 1918, 51, 585.] Similarly *p*-methylcarboxy-benzaldehyde from *p*- $\text{CH}_3\text{O}_2\text{COC}_6\text{H}_4\text{OCl}$.

2912. Benzoyl Chloride: Catalytic Decomposition.¹² Benzoyl chloride when passed with a current of hydrogen over finely divided nickel at 270° C. furnishes to the extent of about 50 per cent a mixture of benzene, toluene, and about 40 per cent of diphenyl. The mechanism of the formation of the latter is obscure, but it appears to be conditioned by the formation of nickel chloride on the surface of the catalyst, and is not suppressed even when an excess of hydrogen is employed. With copper as catalyst benzoyl chloride is decomposed up to about 40 per cent into benzoic anhydride, the remainder being unchanged. A similar conversion occurs at 420° – 450° C., with the chlorides of barium and thorium, with simultaneous deposition of carbon on the catalyst, and formation of carbon monoxide and hydrogen chloride. The manner of formation of the anhydride remains uncertain.¹³

2913. *m*-Fluorobenzoyl chloride to *m*-fluorobenzaldehyde. Xylene solution: Palladium on barium sulphate catalyst (60 per cent yield). [Shoesmith, Sosson and Slater, *Journ. Chem. Soc.*, 1926, 2760.]

2914. 1-Phenyl-5-methyl-1 : 2 : 3-triazole-4-carboxyl chloride on reduction gives 1-phenyl-5-methyl-1 : 2 : 3-triazole-4-aldehyde. 1-Phenyl-5-methyl-1 : 2 : 3-triazole and 1-phenyl-4 : 5-dimethyl-1 : 2 : 3-triazole are by-products. Impure hydrogen causes formation of anhydride of 1-phenyl-5-methyl-1 : 2 : 3-triazole-4-carboxylic acid. 1 : 5-Diphenyl-1 : 2 : 3-triazole-4-carboxyl chloride gives 1 : 5-diphenyl-1 : 2 : 3-triazole-4-aldehyde.

2915. Hydrogenation of *sym.* phthalic chloride in tetralin with palladium-kieselguhr catalyst at 150° , with varying amounts of quinoline-*s* as "regulator," showed but little specific influence of the regulator. The filtrate treated with phenylhydrazine, etc., according to the usual technique, gave phenyl-1-hydroxyphthalazine. From the residue after evaporation in vacuo, phthalide was obtained by water extraction: the catalyst, extracted with hot glacial acetic acid, gave biphtalide.

⁸ *Brit. Chem. Abst.*, 1926, 405A.

⁹ K. W. Rosenmund, *Ber.*, 1918, 51, 585–594.

¹⁰ See further *J. Chem. Soc.*, 1918, i, 300.

¹¹ *Brit. Chem. Abst.*, 1918, 442A.

¹² Mailhe and de Godon, *Bull. Soc. Chim.*, 1916, 19, 449–452.

¹³ *J.S.C.I.*, 1917, 129.

2916. Benzyl-, methylbenzyl-, diethyl-malonyl-chlorides could not be reduced to the malonic dialdehydes by this method. Reduction occurred with a yield of oils with no aldehydic properties. Scarcely more successful were attempts to prepare dialdehydes of pyridinecarboxylic acids. This is attributed to the fact that the acid chlorides form double compounds with POCl_3 , which are catalyst poisons. One such compound with collidinedicarboxylic acid chloride on hydrogenation in xylene or ethyl benzoate gave 15 per cent of aldehyde.¹⁴ [Zetsche, Flütsch, Enderlin and Loosli, *Helv. Chim. Acta*, 1926, 9, 182.]

2917. Gallaldehyde is produced by Rosenmund's hydrogenation method. The carbomethoxy- and the acetyl derivatives of gallic acid are converted into the chlorides and these in cumene or xylene solution are hydrogenated in presence of a palladium-barium-sulphate catalyst (or of Kelber's nickel catalyst) to: 3 : 4 : 5-trimethoxycarboxybenzaldehyde and 3 : 4 : 5-triacetoxycarboxybenzaldehyde, which on hydrolysis yield gallaldehyde, 3 : 4 : 5-tri-hydroxybenzaldehyde. [Rosenmund and Zetsche, *Ber.*, 1918, 51, 594.] With reagents of high purity an intermediate product from the acetyl compound can be isolated—triacetyl-gallic aldehyde. [Rosenmund and Pfannkuch, *Ber.*, 1922, 55, 2357.]

2918. 3-Methyl-carboxy-4 : 5-dimethoxybenzoic acid chloride to 3-methyl-carboxy-4 : 5-dimethoxybenzaldehyde. [Mauthner, *Annalen*, 1926, 449, 102.]

2919. 5-Methoxy- α -naphthoyl chloride to 5-methoxy- α -naphthaldehyde (5 g.) in xylene (25 cc.) in contact with palladinized barium sulphate was reduced by a current of dry hydrogen for four hours, the temperature of the bath being 170° C. [Cf. Rosenmund, *Ber.*, 1918, 51, 591.]¹⁵

2920. 3 : 4 : 5-Trimethoxybenzoyl chloride to 3 : 4 : 5-trimethoxybenzaldehyde. 25 g. of the chloride in 100 cc. dry xylene, 5 g. palladinized barium sulphate, six hours in a slow stream of hydrogen. [Baker and Robinson, *J. Chem. Soc.*, 1929, 156.]

2921. Brombenzene to benzene. Liquid phase : colloidal palladium catalyst or palladinized barium sulphate : boiling under reflux. [Rosenmund and Zetsche, *Ber.*, 1918, 51, 579.]

2922. Bromstyrene to ethyl-benzene. Liquid phase : colloidal palladium catalyst. [Borsche and Heimbürger, *Ber.*, 1915, 48, 452.]

2923. Iodobenzene to benzene and some diphenyl. Gas phase : 270° : nickel catalyst. The method is unsatisfactory; the reaction soon stops, owing to the formation of nickel iodide, which cannot be reduced by the hydrogen in the presence of iodobenzene. [Sabatier and Mailhe, *Compt. rend.*, 1904, 38, 245.]

2924. Chlorinated benzenes to carboxylic acids. Vapor phase : Nickel catalyst on carrier (pumice) : carbon monoxide gas. By introduction of ammonia, aniline and para-toluidine result. [Dieterle and Eschenbach, *Arch. Pharm.*, 1927, 265, 187; *Chem. Abst.*, 1927, 21, 1975.]

2925. *m*-Chlortoluene to methyl-chlorocyclohexane. Glacial acetic acid solution : platinum-black catalyst. [Willstätter and Hatt, *Ber.*, 1912, 45, 1471.]

2926. Chlornitrobenzenes to aniline hydrochloride. Gas phase : 270° : nickel catalyst. [Sabatier and Mailhe, *Compt. rend.*, 1904, 138, 245.]

2927. With copper catalyst at 360°–380°, the chloranilines are formed. [Mignone, *Bull. Soc. Chim.*, 1910 (4), 7, 270.]

2928. Chlorcrotonic acid to crotonic acid. Liquid phase, boiling under reflux : colloidal palladium catalyst. [Rosenmund and Zetsche, *Ber.*, 1918, 51, 579.]

2929. *o*- and *p*-Methoxybenzyl chlorides to *o*- and *p*-xylenes. The mixture of the methoxybenzyl chlorides is prepared by treating toluene with formaldehyde in presence of hydrochloric acid and a condensing agent, e.g., zinc chloride.¹⁶

2930. Sebacyl dichloride to decanedial (sebacyl dialdehyde). Boiling xylene solution : palladium-calcium carbonate catalyst. [Waser, *Helv. Chim. Acta*, 1925, 8, 117.]

¹⁴ *Chem. Abst.*, 1926, 20, 1226.

¹⁵ *J. Chem. Soc.*, 1926, 3242.

¹⁶ *Brit. Pat.* 300,940, Aug. 20, 1927, to Carpmael (from I. G. Farbenind. A.-G.); *Brit. Chem. Abst.*, 1929, 123B.

2931. *o*-Chlorbenzoic acid to benzoic acid. Liquid phase, boiling under reflux : colloidal palladium catalyst. [Rosenmund and Zetsche, *Ber.*, 1918, **51**, 579.]

2932. Chlorcinnamic acid to cinnamic acid. Liquid phase, boiling under reflux : colloidal palladium catalyst. [Rosenmund and Zetsche, *Ber.*, 1918, **51**, 579.]

2933. Triphenylacetyl chloride to triphenylmethane. Palladinized barium sulphate. (Expected aldehyde was not obtained.) [Danilov and Venus-Danilova. *Ber.*, 1926, **59B**, 377.]

2934. Orsellinic Acid Synthesis.¹⁷ Ethyl methylhydroresorcylate, prepared by the condensation of ethyl crotonate with ethyl aceto-acetate in the presence of sodium ethoxide, is converted by bromine in glacial acetic acid into ethyl dibromo-orsellinate, m.p. 143-144°, which is transformed by hydrogen in the presence of palladium and calcium carbonate into ethyl orsellinate, m.p. 132°; hydrolysis of the ester by cold sodium hydroxide affords orsellinic acid identical with the natural product.¹⁸

2935. Dibrom-*n*-propyl-resorcin-carboxylic acid to *n*-propyl-resorcin-carboxylic acid (divaric acid occurring naturally in a lichen). Sodium hydrate 2N-solution : palladium-calcium carbonate catalyst. [Sonn, *Ber.*, 1928, **61B**, 2480.]

2936. 1, 8-Naphthalyl chloride, $C_{10}H_6(COCl)_2$ on catalytic reduction gave a mixture from which only the anhydride was isolated. [Davies and Leeper, *J. Chem. Soc.* 1927, 1124.]

2937. 2, 4-Dichloro-1, 8-naphthyridine to 1, 8-naphthyridine. [Köller, *Ber.*, 1927, **60B**, 1918.]

2938. Chlormenthol to 3-*p*-menthol. Solution in dilute alcohol : palladium black. [Kötz and Busch, *J. pr. Chem.*, 1928, **119** (ii), 1.]

2939. Phenylchlorocamphor $C_6H_5\begin{matrix} \diagup CO \\ | \\ \diagdown CC(C_6H_5)_2 \end{matrix}$ to phenylcamphor. Solution in a mixture of alcohol, ethyl acetate and water : nickel catalyst. [Rupe, *Verh. Naturforsch. Ges., Basel*, 1927, **38**, 164.]

2940. Dehalogenation of Thyroxin. Thyroxin, 1 per cent solution in normal potassium hydroxide, is shaken, in hydrogen, with a palladium-calcium carbonate catalyst. The iodine is removed and an equivalent quantity of hydrogen taken up. The product was shown (by synthesis and degradation) to be: α -amino- β -4-(*p*-hydroxyphenoxy) phenylpropionic acid, $HO \cdot C_6H_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot CH(NH_2) \cdot COOH$. [Harrington, *Biochem.*, 1926, **20**, 300.]

2941. Sodium-bromobenzenesulphonate, 2-chloro-*p*-cymene-3-sulphonate or other halogenized aromatic sulphonic acid containing halogen in the aromatic nucleus, in aqueous alkaline solution, is subjected to the action of hydrogen and a hydrogenating catalyst, such as a nickel catalyst, at temperatures of 20°-300° C.¹⁹

¹⁷ Sonn, *Ber.*, 1928, **61B**, 926.

¹⁸ *Brit. Chem. Abst.*, 1928, 756A.

¹⁹ U. S. Pat. 1,645,974, Oct. 18, 1927, to Schöllkopf; *Chem. Abst.*, 1928, **22**, 91.

CHAPTER XXX

MISCELLANEOUS HYDROGENATIONS CHIEFLY OF BIOCHEMICAL INTEREST

HYDROCARBONS ¹

3000. Squalene. Squalene is a hydrocarbon found in surprisingly large quantities in the liver oils of certain sharks. For the hydrogenation of squalene, see Tsujimoto, *Ind. Eng. Chem.*, 1916, **8**, 889; Chapman, *J. Chem. Soc.*, 1917, **111**, 56; 1923, **223**, 769; Heilbron, Hilditch and Kamm, *J. Chem. Soc.*, 1926, 3131; Heilbron and Thompson, *J. Chem. Soc.*, 1929, 883. The principal product is dodecahydrosqualene.

3000A. By the hydrogenation of spinacene, a hydrocarbon from certain fish-liver oils, with platinum-black as catalyst, Chapman ² found the iodine value was reduced to 18, and a hydrocarbon, $C_{30}H_{52}$, boiling at 274° to 275° C. (18 mm.) was obtained. This was a colorless, odorless oil not solidifying at - 20° C., and having a specific gravity of 0.8172 at 20°-20° C. The unsaturated hydrocarbon squalene separated by Tsujimoto closely resembles spinacene.

3001. Kurozame oil (from the liver of the black shark, mainly of the genus *Zamurus*) on hydrogenation in the presence of a nickel catalyst yields a product, m.p. 46°-47°, acid value 3.2, saponification value 82.8, iodine value 1.2, unsaponifiable matter 51.43 per cent. The unsaponifiable portion contains dodecahydrosqualene (for which the name squalane is suggested), batyl alcohol, derived chiefly from selachyl alcohol [*cf. J. Chem. Soc.* 1922 (i), 297], and probably hydrogenated cholesterol. Dodecahydrosqualene as isolated from the crude hydrogenated product by distillation is a colorless liquid of very low volatility, b.p. 272°/15 mm., d_4^{20} 0.8084; n_D^{20} 1.4515; flash-point (Pensky-Martens apparatus) 190°. It is unchanged by treatment with sulphuric acid at 70°. ³ [Tsujimoto, *Chem. Umschau*, 1927, **34**, 256.]

3002. Hydrocarbon from Resin Acids of Hops. The hydrocarbon $C_{16}H_{14}$ (from humulic acid by reduction) gives 1 : 3-diisomyrcyclopentane on hydrogenation glacial acetic acid in presence of Adams platinum oxide catalyst, but not of platinum-black or of platinum sponge. [Note paragraph 2786, page 294. Wieland and Martz, *Ber.*, 1926, **59B**, 2352.]

STEROLS

3003. Cholesterol to dihydrocholesterol. Ether solution : 33 per cent (by weight of substrate) of platinum-black catalyst : two days. [Willstätter and Meyer, *Ber.*, 1908, **41**, 2199.]

3004. Cholesterol to dihydrocholesterol. Acetone solution : palladium catalyst.

3005. Cholesterylene absorbs also only 2 atoms of hydrogen. [Nord, *Biochem. Z.*, 1919, **99**, 261; *Chem. Abst.*, 1920, **14**, 2163.]

3006. Cholesterol to cholestane. Ether solution : platinum-black catalyst. [Steinkoff, Winternitz, Roederer and Wolynski, *J. prakt. Chem.*, 1919, **100**, 65; *Chem. Abst.*, 1920, 3635.]

¹ For hydrogenation of caoutchouc, etc., see para. 3070 *et seq.*

² *J. Chem. Soc.*, 1917, 56.

³ *Brit. Chem. Abst.* 1927, 105.

3007. Cholesterilene to cholestan and pseudo-cholestan. Palladium catalyst. [Fantl and Kabos, *Monatsh.*, 1926, **47**, 251; *Chem. Abst.*, 1927, **21**, 590.]

3008. Allocholesterol to coprosterol (with some dihydrocholesterol). In amyl ether solution. Allocholesterol is formed by boiling cholesterol hydrochloride with anhydrous sodium acetate in absolute alcohol. When cholesterol is heated with nickel at 180° C. an internal hydrogenation of the double bond occurs at the expense of the alcohol group, with the formation of ketones (cholestanone, coprostanone). [Windaus, *et al.*, *Ann.*, 1927, **453**, 101; *Chem. Abst.*, 1927, **21**, 2905.]

3009. The formation of these ketones, in which allocholesterol is probably an intermediate stage, explains the hydrogenation of cholesterol to γ -cholestanol. The latter is also obtained by heating cholesterol at 180° with alcoholic sodium ethoxide. The reduction of a double linking under these conditions is abnormal and may again be due to intermediate formation of cholestanone and coprostanone. β -Cholesterol is catalytically hydrogenated in ether-glacial acetic acid to dihydrocholesterol. If it differed from cholesterol in the configuration of the hydroxyl group, ϵ -cholestanol should be formed, so that probably only the position of the double linking is different.⁴ [*Ibid.*]

3010. α - and β -Sitosterol to sitostanol $C_{27}H_{47}OH + H_2O$.

3011. γ -Sitosterol to γ -sitostanol. Platinum-black catalyst. [Anderson and Shriner, *J. Biol. Chem.*, 1927, **71**, 401-406. See also: Anderson, Shriner and Burr, *J. Amer. Chem. Soc.*, 1926, **48**, 2987; Bonstedt, *Z. physiol. Chem.*, 1928, **176**, 269.]

3012. *l*-Sitosterol to *d*-dihydrositosterol (sitostanol, $C_{27}H_{47}OH$), with Voorhees-Adams' platinum oxide catalyst; sitosterol 10 g., ether 300 cc., 0.65 g. catalyst. [Anderson and Nabenhauer, *J. Am. Chem. Soc.*, 1924, **46**, 1953.]

3013. Phytosterols. When β -sitosterol is reduced with hydrogen and platinum-black, dihydro- β -sitosterol is formed. The properties of this compound differ from those of dihydro- γ -sitosterol. It melts at 140°-141°; $[\alpha]_D + 24.91^\circ$.

3013A. Sterol mixtures apparently rich in α -sitosterol are reduced with great difficulty by hydrogen and platinum-black, but the reduction product which is finally obtained appears to be identical with that prepared from β -sitosterol. The substance melted at 139°-140°; $[\alpha]_D + 23.53^\circ$.

3013B. α -Sitosterol differs from β -sitosterol in forming a bromine substitution product which cannot be debrominated. The two compounds must be closely related, nevertheless, since both give saturated sterols on reduction which are identical in composition and have very similar properties. It is interesting to note that the melting-points and rotations of these reduction products are very similar to those of the natural dihydrositosterol. [Anderson and Shriner. The phytosterols of corn oil. *J. Am. Chem. Soc.*, 1926, 2978.]

3014. Dihydro- γ -sitosterol. Both γ -sitosterol preparations were reduced with hydrogen in the presence of platinum-black. The reduction products had similar properties: (1) m.p. 143°-144° $[\alpha]_D + 18.89^\circ$; (2) m.p. 143°-144° $[\alpha]_D + 18.01^\circ$. The acetyl derivative melted at 142°-143° $[\alpha]_D + 9.98^\circ$. [*Ibid.*, p. 2993, The phytosterols of wheat germ oil.]

3015. Ergosterol (acetate) from yeast, to α -ergosterol (acetate). Liquid phase: platinum gauze catalyst. Reduction with Adams' platinum catalyst gives a mixture of the α -ergosterol acetate and the acetate from the pure sterol. [Reindel and Walter, *Ann.*, 1928, **460**, 212; *Chem. Abst.*, 1928, **22**, 1593; see Heilbron and Sexton, *J. Chem. Soc.*, 1929, 921.]

3016. α -Ergosterone to α -ergosterol.

3016A. *Allo*- α -ergosterone to *allo*- α -ergosterol and a new isomeric sterol, not precipitable by digitonin, and not having anti-rachitic properties even when irradiated. [Reindel (with others), *Ann.*, 1928, **466**, 131; *Brit. Chem. Abst.*, 1929, 61A.]

3017. A neutral compound $C_{28}H_{48}(\text{or } 46)O_4$, obtained by oxidation of ergosterol on catalytic hydrogenation yields a compound $C_{28}H_{44}(\text{or } 42)O_3$, by absorption of 3 molecules of hydrogen and elimination of water. [*Idem, ibid.*]

⁴ *Brit. Chem. Abst.*, 1928, 557.

3018. Vitamin A: Hydrogenation of "Biosterin."⁶ On reduction of biosterin by Fokin and Willstätter's method, a solid substance separates, in which nonacosane, batyl alcohol, octadecyl palmitate, and melissyl alcohol have been detected. The greater portion of the product is, however, liquid at the ordinary temperature, and can be separated by distillation into two fractions; it is not possible to ascertain which of these corresponds with vitamin A, as the activity is destroyed by the reduction.

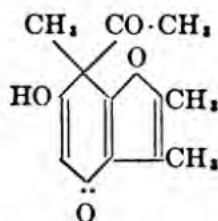
3018A. The Fokin and Willstätter method referred to is possibly that described by Willstätter and Mayer⁶ with a reference to Fokin. The sterols, etc., are dissolved in ether and hydrogenated at room temperature with a platinum catalyst. Recent opinion tends to the belief that, under these conditions, vitamin A is stable. It is possible that, following Willstätter's later practice, Nakamiya and Kawakami may have introduced oxygen: to this the vitamin is highly sensitive.

3018B. Sumi⁷ affirms that hydrogenation destroys the antirachitic property of irradiated ergosterol. If this is true it appears to be so only of the concentrated and perhaps only of the irradiated product. Naturally occurring vitamin D (anti-rachitic) in conditions of hydrogenation (as when cod-liver oil is hydrogenated at room temperature to a solid fat) does not seem to lose the antirachitic property.

3019. Selachyl alcohol (from the liver oil of elasmobranch fish) to batyl alcohol. Platinum-black catalyst (Chapman). Nickel catalyst at 150° C. [Heilbron and Owens, *J. Chem. Soc.*, April, 1928, 947.]

3020. Phytol, $C_{20}H_{40}OH$, to dihydrophytol, $C_{20}H_{42}OH$. Liquid phase: platinum-black catalyst. [Willstätter and Mayer, *Ber.*, 1908, **41**, 1475.]

3021. Usnetol, $C_{13}H_{14}O_4$ (from usnic acid derived from *Usnea barbata*, a lichen) to dihydrousnetol. Glacial acetic acid solution: palladium catalyst. Usnetol appears to be an enol:



[Schöpf, Heuck and Kraus, *Ann.*, 1927, **459**, 233; *Chem. Abst.*, 1928, **22**, 1589.]

OTHER COMPOUNDS

3022. Brazilin and Hematoxylin Derivatives. 3-*mp*-Dihydroxybenzylidene derivative of 7-methoxychromanone is smoothly reduced by hydrogenation, with a palladium catalyst, to 3-*mp*-dihydroxy-benzyl-7-methoxychromanone together with an unidentified substance, m.p. 139° C. [Perkin, Rây and Robinson, *J. Chem. Soc.*, 1927, 2094.]

3023. Deoxtrimethylbrazilone with a palladium catalyst was reduced to a dehydro-derivative. [*Idem*, *Ibid.*, 1928, 1504.]

3024. Trimethylbrazilone, in glacial acetic acid solution, with a spongy platinum catalyst, at room temperature, is hydrogenated to a dihydroxy-compound. [Pfeiffer, Angern, Haack and Willems, *Ber.*, 1928, **61B**, 1923.]

3025. Tetramethylhematoxylone, similarly hydrogenated, gives an analogous dihydroxy derivative, $C_{18}H_{20}O(OCH_3)_4(OH)_2$. [*Ibid.*]

3026. Trimethylanhydrobrazilin to trimethyldesoxybrazilin.

3027. Tetramethylanhydrohaematoxylin to tetramethyldesoxyhaematoxylin. Plati-

⁶ Nakamiya and Kawakami, *Sci. Papers Inst. Phys. Chem. Res.*, Tokyo, 1927, **7**, 121.

⁶ *Ber.*, 1908, **41**, 1475; *Chem. Abst.*, 1908, 2218.

⁷ *Biochem. Z.*, 1929, **204**, 396; *Chem. Abst.*, 1929, **23**, 1942.

num catalyst. [Pfeiffer, Angern, Haack and Willems, *Ber.*, 1928, 61B, 839; *Chem. Abst.* 1928, 22, 2360.]

3028. 7-Acetoxychromone hydrogenated by Willstätter's method gave 7-acetoxychromanone. [Pfeiffer, Oberlin and Konermann, *Ber.*, 1925, 58B, 1947.]

3029. Capsanthin. $C_{54}H_{80}O_2$ (coloring matter of paprika) is highly unsaturated; on catalytic hydrogenation it takes up 9 molecules of hydrogen. When 6 molecules have been absorbed all the color has disappeared. The hydrogenated product is named perhydrocapsanthin and is a liquid, probably a mixture of stereoisomerides. The hydrogenation is carried out in alcoholic or, better, acetic acid solution, with a platinum catalyst. [Zechmeister and von Chohnoky, *Ann.*, 1928, 465, 288. Cf. hydrogenation of carotin, next paragraph.]

3030. Hydrogenation of Carotin. Carotin $C_{40}H_{56}$ to perhydrocarotin $C_{40}H_{72}$. Cyclohexane or ether solution: spongy platinum catalyst. [Zechmeister, Chohnoky and Vrabély, *Ber.*, 1928, 61B, 566.]

3031. II. [*Ibid.*] Catalytic hydrogenation of carotin in cyclohexane in the presence of platinum shows that its double linkings are divisible into two groups. At least two and probably three of them are distinguished by not being causative of color; they become hydrogenated towards the end of the reaction after the double linkings of the second type have become almost completely saturated. The color of carotin is due to a series of double linkings which readily absorb hydrogen. As long as hydrogenation mainly affects the latter type, the diminution in the intensity of the color of the solution is proportional to the consumption of hydrogen. The color appears to be lost completely after additions of 8 molecules of the gas. Partly hydrogenated solutions of carotin all exhibit the typical carotin spectrum and hence contain a mixture of unchanged material and decolorized products; colored intermediate compounds do not appear to be formed. Carotin therefore appears to contain eight olefinic linkings conjugated with one another and three further double linkings. The optical inactivity of perhydrocarotin appears to ally it closely to perhydro- ψ -crocetin and to strengthen further the analogy between the safran dyes and the carotin group. Perhydrocarotin, $C_{40}H_{72}$, conveniently prepared by catalytic hydrogenation of carotin in chloroform in the presence of platinum, has normal molecular weight in freezing benzene, indicating a C_{40} formula for carotin, which is supported by direct determinations of its molecular weight in freezing benzene and camphor.⁸

3032. Crocetin: α -crocetin is an acid derived from saffron. It is $C_{22}H_{28}O(COOH)_2$, i.e., an aliphatic dicarboxylic acid with eight conjugated double bonds. γ -Crocetin is the dimethyl ester of this acid and on catalytic hydrogenation gives a dimethyl ester $C_{22}H_{40}O(COOCH_3)_2$. [Karrer and Salomon, *Helv. Chim. Acta*, 1928, 11, 513.]

3033. Lycopin⁹ by catalytic hydrogenation forms perhydrolycopin, $C_{40}H_{52}$, and demonstrates its (paraffin) aliphatic constitution and its resemblance to carotin, *q.v.*

3034. Xanthophyll.¹⁰ $C_{40}H_{56}O_2$, is hydrogenated in ethyl or propyl alcohol, ether, chloroform, or glacial acetic acid in the presence of an unusually large amount of spongy platinum to non-crystalline perhydroxanthophyll, $C_{40}H_{72}O_2$. The hydrogenation graph of xanthophyll is very similar to that of carotin, showing a rectilinear progress until 8 molecules of hydrogen have been absorbed and the solution has become colorless. Xanthophyll therefore probably contains eight conjugated double linkings which rapidly become hydrogenated and three sluggish double linkings which are not responsible for the color. It is possible that carotin contains two alkyl and xanthophyll two alkoxy-groups in corresponding positions in the molecule.¹¹

3034A. Bixin, pigment of annatto ($C_{22}H_{30}O_4$ or $C_{22}H_{30}O_4$), dissolved in glacial acetic acid is converted by hydrogen in presence of palladized barium sulphate into perhydrobixin. [Faltis and Vieböck, *Ber.*, 1929, 62B, 701; *Brit. Chem. Abst.*, 1929, 575A.]

⁸ *Brit. Chem. Abst.*, 1928, 1015A.

⁹ Karrer and Widmer, *Helv. Chim. Acta*, 1928, 11, 751.

¹⁰ Zechmeister and Tuzson, *Ber.*, 1928, 61B, 2003.

¹¹ *Brit. Chem. Abst.*, 1928, 1252A.

3035. Catalytic Reduction of Glucosides. Aucubin, $C_{16}H_{24}O_8$, (from fruit of *Aucuba japonica*), on reduction in presence of colloidal platinum, absorbed 4 molecules of hydrogen, giving glucose (1 mol.) and an oil, tetrahydrodesoxyaucubigenin, $C_8H_{20}O_2$. Thus hydrogenation with elimination of water had occurred. With a platinum oxide catalyst at 1.5 atmospheres hydrogen pressure, 3 molecules, only, of hydrogen were absorbed with production of a syrupy substance (? hydroaucubin). [Kariyone and Kondo, *J. Pharm. Soc., Japan*, 1928, **48**, 679; *Chem. Abst.*, 1929, **23**, 393.]

3036. Salicin with colloidal palladium gave *o*-cresyl glucoside, $1,2-CH_2 \cdot C_6H_4O \cdot C_6H_{11}O_5$, so that the reduction took place only on the hydroxyl group.

3037. Arbutin, however, behaved like aucubin and, absorbing 4 molecules of hydrogen, gave hexahydrophenol and glucose. [*Ibid.*]

3038. Anhydrodigitoxigenin to tetrahydroanhydrodigitoxigenin, $C_{21}H_{34}O_4$. [Windaus and Freese, *Ber.*, 1925, **58B**, 2503; cf. Windaus and Stein, *Ber.*, 1928, **61B**, 2438.]

3039. Gitoxigenin, $C_{21}H_{34}O_5$, on hydrogenation appears to yield 2 isomeric dihydrogitoxigenins, $C_{21}H_{36}O_5$. Each is converted by hydrogen chloride in alcohol into dianhydrodihydrogitoxigenin, $C_{21}H_{32}O_5$. This is readily hydrogenated with a platinum-black catalyst to tetrahydrodianhydrodihydrogitoxigenin, a mixture of isomerides from which $C_{21}H_{36}O_5$ is isolated. The oxidation of this gives a ketone (identical with Bandte's hexahydrodigitaligenone), tetrahydrodianhydrogitoxigenone. [Windaus, Westphal and Stein, *Ber.*, 1928, **61B**, 1847.]

3040. Matrine Derivatives. α -Matrinidine gives dihydro- α -matrinidine on hydrogenation in presence of colloidal palladium.

3041. Des-*N*-methyldihydro- α -matrinidine, $C_{11}H_{24}N_2$ gives the tetrahydro derivative.

3042. Des-*N*-dimethyltetrahydro- α -matrinidine (with palladinized charcoal catalyst) gives a hexahydro compound.

3043. Des-*N*-trimethylhexahydro- α -matrinidine gives the octahydro compound. [Kondo, Ochiai and Aihara, *J. Pharm. Soc., Japan*, 1928, **48**, 337.]

3044. Ginkgo biloba Fruit Products. Ginkgolic acid $C_{21}H_{30}(OH) \cdot COOH$ on reduction in presence of platinum- or palladium-black gives $C_{21}H_{34}O_2$ identical with cyclogalliparic acid of Kunz-Krause and Schelle.

3045. Ginkgol, $C_{20}H_{30}OH$, obtained from ginkgolic acid by heating, gives a dihydro-derivative identical with cyclogallipharol.

3045A. Bilobol, $C_{21}H_{32}(OH)_2$ on hydrogenation gives a dihydrobilobol. [Kawamura, *J. Chem., Japan*, **3**, 89.]

3046. Linderan, $C_8H_{10}O_2$, from *Lindera strychnifolia*, takes up 2 atoms of hydrogen on catalytic reduction. A similar substance, linderene, $C_{11}H_{14}O_2$, takes up first $2H_2$ and then apparently with rupture of a furan nucleus, another H_2 is taken up and the ultimate product is $C_{11}H_{18}O$. [Kondo and Sanada, *J. Pharm. Soc., Japan*, 1925, No. **526**, 1047.]

3047. Toad Poison Constituents. Bufagin, $C_{29}H_{48}O_7$ (or $C_{27}H_{44}O_7$, according to Kodama) (from Chinese remedy *senso*), on catalytic hydrogenation gives a mixture of α - and β -tetrahydro derivatives. The di-acetyl derivative gives a mixture of 2 dihydro-derivatives.

3048. Gamobufotalin, $C_{27}H_{44}O_6$ (extraction of skins of 5000 Japanese toads yielded 35 g.), on catalytic hydrogenation gives a hydro-derivative. [Kotake, *Ann.*, 1928, **465**, 1.]

3049. Rotenone (the active constituent of *Derris elliptica*, of unknown constitution) to dihydrorotenone: palladinized barium sulphate catalyst. With platinum the CO group is attacked and a dihydrodeoxyrotenone results.

3050. Rotenol (derived from rotenone, probably a secondary alcohol) with platinum is hydrogenated to dihydrorotenol, $C_{22}H_{36}O_4$.

3051. The acetyl derivative of anhydroderritol (also derived from rotenone), hydrogenated in acetic acid solution, with platinum, gives a dihydro-derivative.

3052. Rotenonone (an oxidation product) in acetic acid solution, with platinum,

hydrogenates to perhydrorotenonone, $C_{12}H_{16}O_4$. [Butenandt (and, in part, Linsert and Botschwar), *Ann.*, 1928, 464, 253.]

3053. Betulin (di-acetate) to dihydrobetulin (di-acetate). Glacial acetic acid solution: platinum catalyst. [Vesterberg, *Ber.*, 1927, 60B, 1535.]

3054. Bile Acids. Dehydrocholic acid to 3, 7, 12-trihydroxy-cholanic acid. Acetic acid solution: Platinum-black: six hours.

3055. 7, 12-Diketocholanic acid to 7, 12-dihydroxy-cholanic acid. Acetic acid solution: platinum-black: one hour.

3056. Bilianic acid to biliobanic acid. Isobilianic acid to reducto-isobilianic acid (hydroxylactone). [Borsche and Frank, *Ber.*, 1926, 59B, 1748; *Chem. Abst.*, 1927, 21, 101. See also: Borsche and Feske, *Z. physiol. Chem.*, 1928, 176, 109; *Brit. Chem. Abst.*, 1928, 1008A.]

3057. Ketcholonic acid (ethyl ester) to 7-ketocholonic acid. Palladium-barium sulphate catalyst. [Schenck and Kirchhof, *Z. physiol. Chem.*, 1927, 163, 120; *Chem. Abst.*, 1927, 21, 1991.]

3058. Hyodeoxycholic acid and α -dehydrohyodeoxycholic acid, on catalytic hydrogenation, both yield 2:13-dihydroxyallocholanic acid. Their oxidation product, hyodeoxybilianic acid (13-ketostadenic acid), on catalytic hydrogenation gives a lactone dicarbocyclic acid.

3059. Lithobilianic acid, $C_{24}H_{38}O_8$, on catalytic hydrogenation, gives allolithobilianic acid. [Windaus, *Ann.*, 1926, 447, 233.]

3060. Dehydrocholic acid gives 3:7:12-trihydroxycholanic acid, differing from natural cholic acid only in its specific rotation.

3060A. Methyl dehydrodeoxycholate gives methyl deoxycholate. Both in glacial acetic acid solution with platinum-black catalyst.

3060B. Similarly hydrogenated 7:12-diketocholanic acid gives 7:12-dihydroxycholanic acid.

3060C. Bilianic (uncertainly) to biliobanic acid. Isobilianic acid to reductoisobilianic acid ($C_{24}H_{38}O_7$). [Borsche and Frank, *Ber.*, 1926, 59 [B], 1748.]

3061. Spermine dehydrogenation product $C_7H_{14}N_2$, when hydrogenated in presence of platinum yields *N*- ω -aminopropylpyrrolidine, $C_7H_{14}N_2$. [Wrede, Fanselow and Strack, *Z. physiol. Chem.*, 1926, 161, 66.]

3062. Psychosine (a base extracted from brain tissue) to dihydropsycho-sine. Palladium catalyst.¹²

3063. Lecithin to hydrolecithin. Absolute alcohol solution: colloidal palladium catalyst. [Paal and Oehme, *Ber.*, 1913, 46, 1297.]

3064. *p*-Acetoamino-*o*-nitro-*m*-cresol methyl ether lodal anhydride, hydrogenated with palladium catalyst. [Shinoda (synthesis of corytuberine), *J. Pharm. Soc., Japan*, 1926, No. 532, 482-489; *Chem. Abst.*, 1927, 21, 2272.]

3065. Alpha-elemic acid, $C_{27}H_{44}O_2$ to dihydroelemic acid, $C_{27}H_{46}O_2$. Alcohol solution: palladium-kieselguhr catalyst. [Bauer, *Ber.*, 1928, 61B, 343.]

3066. Preparation of Adrenin (suprarenin, adrenaline, epinephrin) 3:4-dihydroxy-phenylmethylaminoethanol.¹³ Methylaminoacetyl-3:4-dihydroxybenzene is hydrogenated with metals of the platinum group, in colloidal solution, or finely divided or

¹² Klenk and Härle, *Z. physiol. Chem.*, 1928, 176, 221; *Brit. Chem. Abst.*, 1929, 321A.

¹³ In attempts to isolate the active principle of the suprarenal body Abel prepared its benzoyl compound and believing it to be the pure active principle, named it epinephrin. When by a slight modification of Abel's method, the true active principle was isolated by other workers, it was named adrenaline. This name, however, became a trade-mark. A strong movement was set on foot to give to this product the name epinephrin. Apart from the question of jurisdiction over chemical nomenclature, there seems some impropriety in thus transferring a name from a benzoyl compound to the simple body, as well as some danger of an accusation of partiality.

supported on carbon, or with a nickel catalyst. The yield is almost theoretical and the product of a high degree of purity.¹⁴

3067. Synthesis of Ephedrine. *dl*-Ephedrine. A mixture of 50 cc. of absolute ethyl alcohol, 7.4 g. of methylphenyl diketone (1-20 mole) and an alcoholic solution of methylamine containing 1.6 g. (1-20 mole) was reduced catalytically with hydrogen in the presence of 0.1 g. of platinum oxide. In some experiments there was a long induction period and then the yield was low. This behavior could be obviated by reducing the catalyst first and then adding the reactants.¹⁵

3068. Another and less simple synthesis is covered by Brit. Pat. 302,940, Dec. 23, 1927, to Soc. des Usines chimiques Rhône-Poulenc, assignees of Fourneau. Bromopropiophenone is obtained by direct bromination of propiophenone, and is then treated with methylamine in benzene or alcohol solution to obtain α -methylaminoethylphenylketone. This is hydrogenated, using finely divided platinum as a catalyst to obtain phenyl-methyl-amino-propanol (synthetic ephedrine).¹⁶

3069. Periplogenin, $C_{21}H_{34}O_6$, to a dihydro derivative, $C_{21}H_{36}O_6$. Platinum-black catalyst. Periplogenin is prepared from periplocymarin and the latter from *Periploca graeca*, stems and branches. [Jacobs and Hoffmann, *J. Biol. Chem.*, 1928, **79**, 519; *Chem. Abst.* 1929, **23**, 151.]

3070. Rubber, guttapercha, etc. See: Geiger, *Diss.*, Zurich, 1926; *Gummi-Ztg.*, 1926, **40**, 2143.]

3071. Cyclo-caoutchouc, which may be obtained by heating caoutchouc in ether or benzene solution for a day at 250° C., is converted into a fully saturated compound by hydrogenation in presence of a catalyst, preferably a metal of the eighth group of the periodic system. According to examples the cyclocaoutchouc is triturated with platinum or nickel or copper oxide and treated in a rotary autoclave with hydrogen at 270° C. and 50-80 atmospheres pressure. The product is soluble in benzene, chloroform, and ether, and may be used as a substitute for guttapercha.¹⁷

3072. Crude rubber (not purified) thoroughly "disaggregated" (i.e., made very plastic) in a mixing mill, was dissolved in relatively much petroleum ether. This solution was mixed with platinum-black and subjected, at room temperature, to several atmospheres pressure of hydrogen, forming perhydro-rubber, saturated in respect to bromine. [Harries, *Ber.*, 1923, **56**, 1048; *Chem. Abst.*, 1923, **17**, 2806.]

3073. Rubber is masticated in a vacuum or in an atmosphere of hydrogen and then is hydrogenated with a catalyst. This product is to be used for impregnation and in the making of lacquers and adhesives.¹⁸

3074. The pyrogenic decomposition of guttapercha begins at 285°-290° at 11 mm., becomes vigorous at 300°-315°, and then slackens. The product of such heating is a polycycloguttapercha (C_8H_8)_x, molecular weight (benzene at freezing point), 1950, reduced by hydrogen in presence of nickel at 275°-285°/95 atmospheres to a hydropolycycloguttapercha ($C_{26}H_{42}$)_x, molecular weight 1930.¹⁹

3075. Dehydroprotocantharidin to protocantharidinic acid. Palladium charcoal catalyst. [Bruchhausen and Bersch, *Arch. Pharm.*, 1928, **266**, 697; *Brit. Chem. Abst.*, 1929, 192A.)

3076. The hydrogenation of waxes such as Japan, montan and beeswax is mentioned by Ellis.²⁰

¹⁴ Japanese. Pat. 42,351, to Hoshine and Daiichi Seiyaku Kabushiki Co.

¹⁵ Manske and Johnson, *J. Am. Chem. Soc.*, 1929, **51**, 582. Cf. para. 2696.

¹⁶ *Chem. Age* (London), 1929, **20**, 190.

¹⁷ Brit. Pat. 263,862. International date, Dec. 31, 1925, to Staudinger. *Chem. Age* (London), Mar. 12, 1927, 264; U. S. Pat. 1,654,844, Jan. 3, 1928. See also: Staudinger, *et al.*, *Helv. Chim. Acta*, 1926, **9**, 529 and 549; *Brit. Chem. Abst.*, 1927, 840 and 841A.

¹⁸ Swiss Pat. 121,111, Mar. 22, 1926, to Soc. Chim. Ind., Bâle. The hydrogenation of rubber is mentioned by Ellis in U. S. Pat. 1,345,589, July 6, 1920.

¹⁹ Staudinger and Bondy (with Geiger), *Ann.*, 1929, **468**, 1-57; *Brit. Chem. Abst.*, 1929, 322.

²⁰ U. S. Pat. 1,345,589, July 6, 1920.

CHAPTER XXXI

THE HYDROGENATION OF FATTY OILS

INTRODUCTORY AND HISTORICAL

3100. For years the dream of the oil chemist was to find a solution to the problem of converting oleic acid into stearic acid, or olein into stearin, simply by the addition of hydrogen, so as to make valuable hard fats from relatively cheap raw material. Superficially the problem looked simple. Oleic acid is the next-door neighbor of stearic acid, apparently differing only in having a little less hydrogen than stearic acid has in its constitution. Only a trifling amount of hydrogen, less than 1 per cent, is required to transform oleic into stearic acid.

3101. But the problem was far from simple as oleic acid stubbornly resisted the invasion of hydrogen into its structure to any material extent under the earlier methods of hydrogen addition, and not until later years, with the discovery of effective hydrogen carriers or catalyzers, has it become possible to bring about this conversion economically with large yields so as to warrant commercial exploitation in an extensive way.

3102. Now the problem is solved, and in different parts of the globe dozens of plants turning out daily enormous quantities of "hardened oil," prepared by the treatment of vegetable or other oil with hydrogen have been established. Hydrogenated or hardened oil has taken its place in the oil market as a staple product.

A REVIEW OF THE ART ¹

3103. Many attempts to hydrogenate oleic acid have been made. Reviewing this subject in 1897 ² Lewkowitsch referred to the ease with which the lower members of the oleic series are converted into saturated acids and states that "oleic acid itself resists all attempts at hydrogenization," further remarking that he had "carried out a large number of experiments in this direction under most varied conditions, but hitherto all of these gave negative results."

3104. Prior to this, however, Goldschmidt, in 1875, ³ had reduced oleic acid by means of hydriodic acid and amorphous phosphorus at 200° to 210° C. This

¹ The production of stearic acid and other acids or products of high melting-point from oleic acid is discussed by Hefter, *Technologie der Fette und Öle*, Vol. III, 795 and 994; also by Ubbelohde und Goldschmidt, *Handbuch der Chemie und Technologie der Öle und Fette*, Vol. III, 152.

² *J.S.C.I.*, 1897, 389.

³ *Sitz. b. d. Wiener Akad. d. Wiss.*, 72, 366.

presumably led to the attempted commercial development of a process by de Wilde and Reychler ⁴ involving heating oleic acid to 280° C. with 1 per cent of iodine, adding and melting therein a certain quantity of tallow soap, and then boiling with acidulated water. The product was then distilled and the iodine, in part, recovered from the pitch. The yield of stearic acid or saturated fat is stated to be approximately 70 per cent of the theoretical. Only about two-thirds of the iodine could be recovered so the process apparently did not find technical use.⁵

3105. Chlorine in lieu of iodine was tried, but great difficulty was experienced in securing an autoclave of resistant material. Imbert ⁶ recommended using quantities of chlorine and alkali exactly calculated on the iodine number of the fatty acid and operating at a temperature of 120° to 150° C. and a pressure of about 5 atmospheres for a period of six hours.

3106. Zurrer ⁷ chlorinated the fatty acid and then heated with water in the presence of a finely divided metal, as zinc or iron. Lewkowitsch alleges that the treatment of monochlorstearic acid in this manner causes a reversion to oleic acid.

3107. Tissier, in 1897,⁸ laid claim to a process for the reduction of oleic acid by nascent hydrogen. Powdered metallic zinc is placed in an autoclave, water and the fatty material containing olein being introduced, and treated under pressure. Under these conditions the glyceride is hydrolyzed to fatty acid and glycerine, and according to Tissier nascent hydrogen is evolved by virtue of the finely divided metal and reduces the oleic to stearic acid. Freundlich and Rosaur ⁹ claim the Tissier process to be inoperative.

3108. The conversion of oleic acid into palmitic and acetic acids by means of caustic potash in accordance with the Varrentrapp reaction ¹⁰ did not prove to be commercially practicable, although it was, for a time, in commercial use. One of the causes of its abandonment was the occurrence of hydrogen explosions.

3108A. Experiments by Kalnin reported by Bergius ¹¹ have shown that hydrogenation is effected by heating oleic acid with alkali at 300° C. in hydrogen under a pressure of 30 atmospheres.

As the reaction is not obviously catalytic, it is independent of the purity of the oil or the hydrogen. Simultaneous hydrogenation and saponification, in the absence of catalytic agents Bergius believed would probably prove a cheaper process than that in use. Commenting on this process, Ellis ¹² observes that it is proposed to put this hydrogenated and more or less saponified product directly into the soap kettle and work it up into soap. The high gas pressure required once was considered a drawback from the commercial standpoint.

⁴ *Bull. Soc. Chim.* 1889 [3], 1, 295.

⁵ *Chem. Ztg.*, 1889, 595.

⁶ U. S. Pat. 901,905, Oct. 20, 1908; see also *Bull. Soc. Chim.*, 1899, 695, 707.

⁷ Ger. Pat. 62,407, Aug. 8, 1891.

⁸ French Pat. 263,158, Jan. 16, 1897.

⁹ *Chem. Ztg.*, 1900, 566.

¹⁰ *J.S.C.I.*, (1883) 98, (1884) 200.

¹¹ *Zeitscher. f. angew. Chem.*, 1914, 524.

¹² *Oil, Paint and Drug Reporter*, Oct. 26, 1914, 18.

PROCESSES INVOLVING APPLICATION OF ELECTRICITY

3109. In 1886 Weineck¹³ called attention to the possibility of electrolytic addition of hydrogen to oleic acid. Kuess¹⁴ later attempted to apply the electric current in the steam distillation of fatty acids.

3110. In patents taken out by Magnier, Bragnier and Tissier,¹⁵ the fatty material is acidified with sulphuric acid, whereupon the acidified mass is mixed with 5 to 6 times its weight of water and then under a pressure of 5 atmospheres is subjected to the action of an electric current, which generates hydrogen in a nascent state.

3111. An interesting method of converting oleic into stearic acid is that comprised in the de Hemptinne electric discharge process. The method is carried out by interposing a thin layer of the oil in the path of an electric discharge, while bringing hydrogen into contact with the oil.¹⁶

3112. Figure 26 shows the arrangement of apparatus for this purpose. The conversion is effected in a chamber having an inlet pipe *H*, furnishing hydrogen

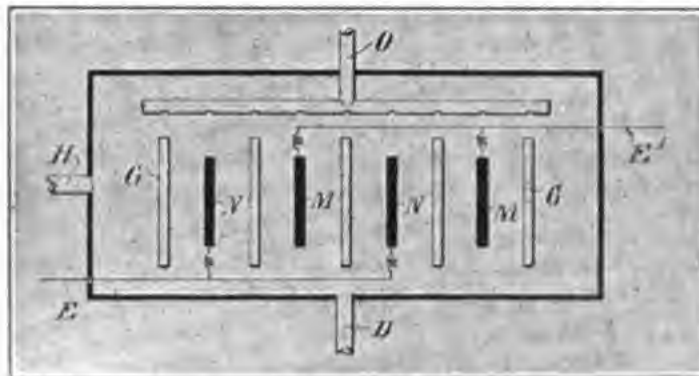


FIG. 26.

under constant pressure. Oleic acid is supplied by a pipe *O* to a sprinkling device which discharges the acid onto a system of parallel plates consisting of the glass plates *G* and alternately the metal plates *M*, *N*. The metal plates *M* are connected to one pole, the others, *N*, being connected with the other pole of a source of electricity. As the oil passes over the plates the electrical discharge causes conversion of some oleic acid into stearic acid, and analogous compounds having melting-points in the neighborhood of 69° C.

3113. de Hemptinne prefers to work at pressures less than atmospheric. The yield is lower at atmospheric pressure. By treatment in this manner it is not difficult to secure a yield of 20 per cent of stearic acid. Repeated treatment permits even up to about 40 per cent yield. Here, as so often elsewhere, the effect of mass action becomes manifest and as the content of stearic acid increases the speed of reaction greatly decreases. Much better results are obtained by satu-

¹³ *Osterr. Privil.*, 10, 400 (July 19, 1886).

¹⁴ *Chem. Ztg.*, 1896, 618.

¹⁵ *Brit. Pat.* 3363, 1900; *Ger. Pat.* 125,446, Oct. 3, 1899, and additional *Ger. Pat.* 132,223.

¹⁶ *U. S. Pat.* 797,112, Aug. 15, 1905; *Brit. Pat.*, 7101, April 4, 1905.

rating to the extent of about 20 per cent, removing the stearic acid by pressing, when the oil of reduced stearic acid content is again subjected to the electric discharge, and a further 20 per cent yield obtained. The oleic residue contains liquid condensation products amounting to about 40 per cent of the total weight. It is stated that the presence of these bodies does not impair the market value of what some one has termed "electrocuted" oleic acid.¹⁷

3114. Petersen¹⁸ also endeavored to reduce oleic acid to stearic acid by allowing an electric current to act between nickel electrodes on an alcoholic oleic acid solution, slightly acidulated with sulphuric acid or preferably with hydrochloric acid. But the yield of stearic acid was small, even under the most favorable conditions, and did not exceed 15 to 20 per cent.

3115. Petersen also endeavored to reduce sodium oleate in aqueous or alcoholic solution to the stearate. No satisfactory results were obtained.

3116. C. F. Böhringer and Söhne¹⁹ obtained by the same method much better results when using, as cathodes, metallic electrodes covered with a spongy layer of the same metal. They recommended as cathodes platinized platinum, and also palladium electrodes covered with a spongy layer of palladium-black. Nickel electrodes were not as effective.

3117. Bruno Waser²⁰ states that oleic acid or olein should be sulphonated and freed from free sulphuric acid before adding hydrogen electrically (cathodic reduction). As an example, one equivalent of oleic acid was mixed with two or three equivalents of 95 per cent sulphuric acid, the temperature not being permitted to advance more than 5 degrees. The mixture was allowed to stand twenty-four hours, was then washed with ice-cold water and dissolved in boiling water. This solution served as catholyte, a 30 per cent sulphuric solution being the anode liquid. A diaphragm separated lead electrodes. The temperature was maintained at 90° to 100° C. with a current density of 25 to 100 amperes per square decimeter, giving 60 to 70 per cent conversion to stearic acid.

CATALYTIC HYDROGENATION OF OILS IN LIQUID PHASE

3118. The first disclosure of the possibility of hydrogenating oils (i.e., glycerides) in the liquid phase seems to have been in the Leprince and Siveke German patent 141,029 of August 14, 1902 (to Herforder Maschinenfett und Oelfabrik) and in the corresponding British patent 1515 of 1903, to Normann. The controversy as to priority, and even as to practicability of the process so disclosed, has now but a historical interest. The reader specially interested in this otherwise obsolete discussion will find details in the 2nd edition of this work, pages 7, 8, 9, and in the Appendix A, which gives an account of the litigation. Chapter XII of this book summarizes that part of the polemic that dealt with the question of nickel *versus* nickel oxide catalysts.

¹⁷ While the de Hemptinne process is of negligible importance as a method of hydrogenating fatty oils, it is interesting because of its relation to the Voltol and similar processes for the production of lubricants dealt with in Chapter LI.

¹⁸ *Z. Elektrochemie*, 1905, 549.

¹⁹ Ger. Pats. 187,788, 189,332, 1906.

²⁰ Ger. Pat. 247,454, March 24, 1911; *Seifrn. Ztg.*, 1912, 661.

CHAPTER XXXII

CATALYTIC HYDROGENATION OF GLYCERIDES AND FATTY ACIDS

EXPERIMENTAL

APPARATUS

3200. In his Inaugural Dissertation, Bedford describes a series of observations made by him prior to or during 1906 on the hydrogenation of oleic acid and certain esters of the fatty acids of linseed oil.¹

An apparatus as shown in Fig. 27 was used to bring oil, hydrogen and catalyzer into contact. The hydrogenating portion of this apparatus consisted of two communicating vertical cylinders k^1k^2 partly filled with catalyzer and immersed in an oil bath. Oil was admitted to one cylinder by means of a dropping funnel while hydrogen was introduced at the bottom

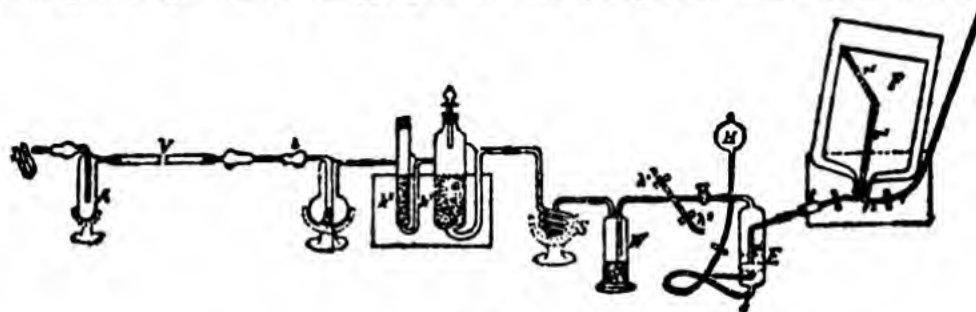


FIG. 27.

of the same cylinder through the glass tube shown on the right hand. The catalyzer was prepared by igniting nickel carbonate to form the oxide, forming the latter into a paste by means of distilled (chlorine-free) water and adding fragments of ignited pumice of about the size of peas. The pumice and nickel oxide paste was well stirred, the material dried at 95° and reduced in the treating apparatus by exposure to hydrogen for eight hours at 275° to 285° C. After reduction the temperature was reduced to 170° to 180° C. and the oil to be hydrogenated was allowed to fall drop by drop on the nickelized pumice while hydrogen was passed through the apparatus. Under these conditions hydrogenation took place and the treated product was duly separated from the catalyzer by extraction with ether. The nickelized pumice thus freed of oil was used again after exposure to hydrogen for one hour at a temperature of 250° C.

3201. Bedford determined the amount of hydrogen absorbed by the unsaturated compounds examined by him in these investigations and expressed his results in part in terms of the "hydrogen number," that is, the percentage of hydrogen absorbed by the compound. When the catalyzer was used for the first time abnormal results were obtained, due, apparently, to the incomplete reduction of the nickel oxide in the preparation of the catalyzer. After using once, more concordant results were secured.

¹ Über die ungesättigten Säuren des Leinols und ihre quantitative Reduktion zu Stearinsäure, Halle, 1906.

3202. Oleic acid having an iodine number of 87.5 was treated in this apparatus and in one trial the reduction product had an iodine number of 4.1 and a melting-point of 64.5° C., while in another case the iodine number was 0 and the melting-point was 69°, indicating the complete transformation of oleic to stearic acid.

3203. Pure oleic acid, according to theory, absorbs 0.714 per cent of hydrogen. This represents the hydrogen number of oleic acid. In two trials Bedford found

	Hydrogen Number Found	Percentage of Theoretical Amount
(A)	0.7226	101.2
(B)	0.7450	104.3

3204. When the ethyl ester of linolenic acid was similarly treated and the hydrogenated product (iodine number, 0) was saponified, stearic acid of melting-point 69° C. was obtained.

3205. The hydrogen number of the ethyl ester of linolenic acid is 1.9737 and the results obtained by Bedford were as follows:

	Hydrogen Number Found	Percentage of Theoretical Amount
(A)	1.9482	98.7
(B)	2.0408	103.4

3206. Bedford also hydrogenated the ethyl esters of the fatty acids of linseed oil (free from oleic acid) and obtained products having numbers ranging from 24.9 to 0. The ethyl ester of stearic acid was the main product of the reaction. The hydrogen number of the ethyl ester of linolenic acid is, as stated, 1.9737, while that of linolic acid is only 1.3072. The hydrogen values found were intermediate these values.

	Hydrogen Number Found
(A)	1.4544
(B)	1.4578
(C)	1.4441

3207. The complete apparatus used by Bedford as shown in Fig. 27 is as follows: The glass container *F* of about 18 liters capacity is used for holding and measuring the hydrogen. The mouth of the container is closed with a stopper having two perforations through which the tubes *r*¹ and *r*² are inserted. The receptacle is surrounded with a metal jacket holding water which enables the temperature to be maintained at the desired point. From the container *F* the tube *t* leads to an intermediate vessel *E*. *H* is a funnel containing water, *W* is a wash-bottle containing sulphuric acid. Hydrogen is introduced at *h*² and nitrogen at *h*¹. *S* is a glass coil cooled by liquid air which serves for the removal of the last traces of moisture from the gases. The catalyzer as indicated above is placed in the vessels *k*¹ and *k*². The vessel *B* is cooled with liquid air. A calcium chloride tube *b* is placed intermediate the latter and the tube *V*. Copper oxide is introduced into the tube *V* and in this tube the hydrogen is converted into water and the latter is condensed in the receptacle *A* by chilling with liquid air. A calcium chloride tube is also connected with the exit of the vessel *A*.

3208. A laboratory method for the hydrogenation of oleic acid is described by Dubovitz.² The hydrogen employed is prepared from arsenic-free zinc and is purified by passing it successively through a mixture of ferric oxide and saw-dust, potassium bichromate and sulphuric acid, sodium hydroxide solution, a tube containing palladium, and concentrated sulphuric acid. Nickel catalyst on pumice is packed into a tube 163 cm. in length. Oleic acid, dried previously at 110° C., is contained in a flask connected with one end of the tube. The air

² *Seifen. Ztg.*, 1915, 304; *J. Chem. Soc.*, 1915, 1049; *J.S.C.I.*, 1916, 127.

is exhausted from the whole apparatus, and hydrogen is passed through the oleic acid heated at 270° C. The tube containing the catalyst is heated at 300° to 350° C. The hydrogen bubbling through the oleic acid carries with it a quantity of oleic acid vapor (a low pressure being maintained in the apparatus) and the gaseous mixture passes into the tube containing the catalyzer, where hydrogenation of the oleic acid takes place.

3209. Successful results are said to depend on (1) the purity of the reagents used in making catalyzer. (2) The construction of apparatus. (3) The skill and experience of the chemist.³

3210. For the reduction of oils with hydrogen under a pressure of 9 atmospheres, an apparatus was constructed by Hamburger,⁴ resembling the one described by Stuckert and Enderli.⁵ The influence of temperature, pressure, divisibility of the catalyst, and kind of oil (impurities therein) on the hydrogenation process was investigated. The hydrogenation of all pure oils with finely divided nickel, as a catalyst, proceeds without difficulty; the same holds true for fatty acids obtained from very impure oils by distillation, with steam vacuum. The nickel catalyst was obtained by the reduction at 260° to 300° of nickel oxide, which had been previously precipitated on pumice stone. It appears, according to Hamburger, that tungsten, molybdenum, thorium, uranium, zirconium, titanium, vanadium and manganese cannot be used as catalysts in the hydrogenation of oils. He states that the claims by Ellis⁶ could not be confirmed, not even when a hydrogen pressure of 200 atmospheres was applied.⁷

3211. Pressure Hydrogenation Apparatus for Laboratory Use. Steingroever⁸ describes an autoclave of 3 liters capacity for the hydrogenation of oils under 20 atmospheres pressure. The autoclave, which is horizontal, is provided with agitator, thermometer, pressure gauge, sight glass, gas inlet and outlet and oil draw-off. The apparatus permits of continuous operation.

3212. Shaking Apparatus for the Determination of Hydrogen Absorption by Oil. A board 8 inches square by about 1 inch thick fastened to a firm bench carries an upright iron rod. Mounted on the board is an electric hot plate and on the hot plate is an enamelware cup large enough to contain a 1-liter flask. The enameled cup and hot plate are surrounded by sheet asbestos for heat insulation. The flask is held in position by a clamp attached to the iron rod. The entire apparatus is held in a horizontal position when at rest by means of springs mounted at each corner of the board. The flask is closed by means of a three-holed rubber stopper, a thermometer being inserted in one of the holes; the thermometer should be long enough that its bulb is immersed in the oil and that the graduations on the thermometer from 180° C. upwards project above the top of the stopper. Quarter-inch glass tubing is connected with the hydrogen supply at one end and projects under the surface of the

³ *Seifen. Ztg.*, 1915, 398, contains Normann's comment on Dubovitz apparatus and method.

⁴ *Chem. Weekblad*, 1916, 13, 2-13; *Chem. Abs.*, 1916, 826.

⁵ A bomb provided with a stirrer for the intimate mixing of a liquid and gas under high pressure and temperature, designed to keep the liquid saturated with the gas as the reaction proceeds. A form of valve for reducing pressures is also described. (*Z. Electrochem.*, 19, 570.)

⁶ U. S. Pat. 1,026,156, May 14, 1912.

⁷ The observations of Hamburger are not in agreement with the results of other investigators. A number of the bodies described by Hamburger as having no catalytic properties have been found to serve as activators or co-catalysts in conjunction with nickel and the like. Some of these are especially active in high-pressure hydrogenations.

⁸ *Z. deut. Oel-Fett-Ind.*, 1926, 46, 338.

oil except during the preliminary flushing with hydrogen. An outlet tube just projects through the stopper and is connected with a bottom outlet aspirator bottle by means of rubber tubing. This has a tee rather close to the aspirator bottle which serves as an outlet for the hydrogen not absorbed when flushing out the flask and during the five-minute running periods. The aspirator bottle is filled with water having an oil layer about 2 inches deep floating on top. The layer of oil serves to prevent the hydrogen from taking up water and should be of this depth to prevent the water coming up far enough to wet the sides of the bottle which come in contact with the hydrogen supply. The bottom outlet of the aspirator bottle is connected with a 100-cc. buret which serves to measure the volume of hydrogen absorbed.

3213. Operation of the Apparatus. 250 g. of prime summer yellow cottonseed oil is weighed out in the flask: 1.25 g. of catalyst, based on the nickel content, is then added to the oil and the temperature of the oil brought up to 180°-190° C. The hot plate is regulated so as to maintain the temperature of the oil between 180°-190° C. After the oil has reached the desired temperature a strong stream of hydrogen is passed for thirty seconds to flush the air out of the flask and replace it with hydrogen. During the flushing of the flask the outlet on the tee in the outlet line is open. When a reading is to be made the rubber tubing on the outlet of the tee is closed by means of a screw clamp, the hydrogen inlet is pushed well down, and a measured quantity of hydrogen is allowed to flow into the aspirator bottle. It is necessary to have the water and the oil in the aspirator bottle completely fill the bottle and it is advisable to fill and empty the aspirator bottle with 100 cc. of hydrogen several times in order to flush out the tube between the tee and the aspirator bottle. The measured quantity of hydrogen is then allowed to flow into the bottle and the apparatus shaken back and forth. The time required to absorb the 100 cc. of hydrogen is taken by means of a stopwatch. The outlet tube on the tee is then opened and a slow stream of hydrogen allowed to pass for a period of five minutes when the time required to absorb 100 cc. of hydrogen is again determined, the results being plotted.

3214. In preliminary experiments a thermometer measured the temperature of the gas in the flask as well as the oil and there was also a thermometer inserted in the aspirator bottle to measure the temperature of the gas there. It was, however, found unnecessary to measure these temperatures as the temperature of the gas in the flask was about 2° lower than the temperature of the oil, while the temperature of the gas in the aspirator bottle was about room temperature. The slight variation of the temperature of the gas in the aspirator bottle, which is really the temperature of the gas that is absorbed, is so small during the course of a day's run that it does not make much difference in the results. The gas in the aspirator bottle is measured by leveling the liquid in the aspirator bottle and maintaining the levels of the liquid throughout the absorption until the 100-cc. point is reached when the time is taken. A reducing valve with needle valve is used for regulating the flow of hydrogen into the flask. The flow of hydrogen during the five minutes' running time is measured by the eye, i.e., by the way the bubbles come through the oil. A very rapid flow makes little difference in the curve plotted. A too slow flow, however, say 100 cc. per minute through the oil, does make some difference, owing to the fact that the catalyzer settles to a certain extent in the oil. A flow of about 500-1000 cc. per minute is suitable. It requires two operators to take the readings, one to shake the apparatus and note the time required to absorb the hydrogen and the other one to level the liquids in the buret and the aspirator bottle.

3215. Some manufacturers of oil-refining machinery make miniature plants with which all the operations of refining, deodorizing and hydrogenation can be carried out on an experimental scale.

3216. Hydrogen Value: Method and Apparatus. The hydrogen value is proposed by Fokin⁹ as a means of determining unsaturated organic compounds in a manner similar to the iodine values of Hubl and Wijs. The "hydrogen value" of an organic compound is defined as the number of cubic centimeters of hydrogen (at 0° C. and 760 mm.), which are absorbed by 1 g. of the compound. For the test an apparatus is devised consisting of a distillation flask (50

to 150 cc.) having a small beaker fused inside on the bottom, and connected by means of the side tube to a gas buret and a gasometer containing hydrogen. In the small beaker is placed about 0.1 g. of catalytic platinum, moistened with $\frac{1}{2}$ cc. of water, and in the flask the substance to be examined and 20 to 30 cc. of alcohol free from dissolved oxygen. Hydrogen is admitted and the flask is shaken by a shaking machine until absorption is complete. The following hydrogen values were obtained by Fokin, the figures in parentheses being either the hydrogen values corresponding with Wijs' iodine value, or, where indicated, the theoretical hydrogen values. Elaidic acid, 78.6 to 81.4 (78.8); oleic acid, 86.2 to 87.2 (86.2); fatty acid from sunflower oil, 119.6 to 120.8 (122.9); fatty acids from linseed oil, 164.9 to 166.3 (166.0); castor oil, 73.7 (75.5); croton oil, 260.9

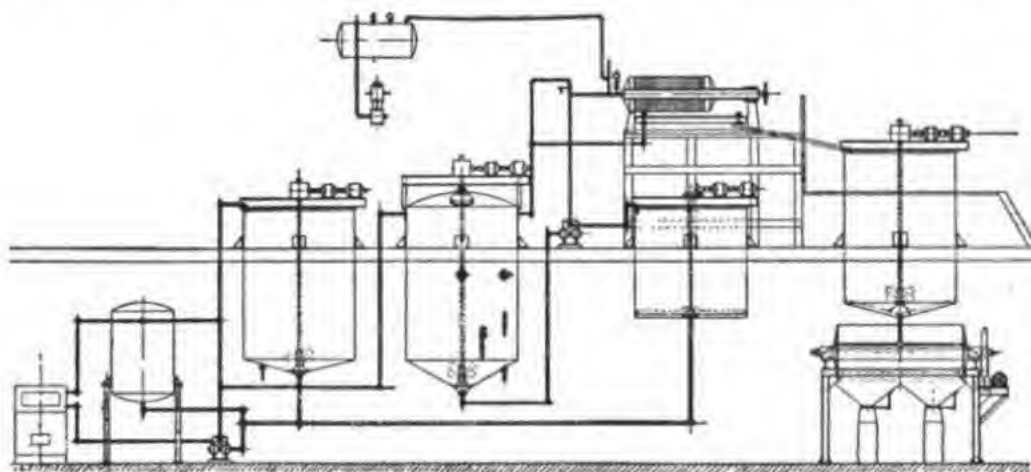


FIG. 28.—HYDROGENATION EQUIPMENT.

Catalyst prepared in the reducing furnace and tank shown at the extreme left is pumped to a mixing tank, above and a little to the right. From here the oil mix is pumped into a converter, and there hydrogenated. This mixture is pumped through a filter press and the clear product is run into a hardened oil storage tank, preparatory to being fed over a roll, where the product is cooled and obtained in flake form. After a batch has been run through the filter press, the latter is opened and the catalyst dropped into the catalyst mixing tank. In this way the same catalyst may be used many times if well-refined oils are being subjected to hydrogenation. (Courtesy of the Albright-Nell Company.)

(theoretical, 258.4); undecic acid, 115.6 (114.1); erucic acid, 39.4 (65.6). Colophony does not absorb hydrogen under the conditions of the test.⁹

3217. The determination of the hydrogen number is described by Albright¹⁰ and although his investigations are concerned mainly with essential oils, the data secured are of interest in connection with the examination of fatty oils. A form of colloidal palladium was used as a catalyst¹¹ and a method of preparing material of this character is given by Albright.

3218. The apparatus used by Albright, which is shown in Figs. 29 and 30, is similar in principle to that devised in the organic laboratory of the University of Göttingen. Its funda-

⁹ *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 700; *J. Chem. Soc.*, 1908, Abst. ii, 637.

¹⁰ *J. Am. Chem. Soc.*, 1914, 2188.

¹¹ Paal and Amberger, *Ber.*, 1904, **37**, 124.

mental parts are the camshaft, carrying four eccentrics; the shaking baskets *A*, attached to the cams and suspended from pulleys on a supporting rod; the absorption flasks *B*, which are placed in the wire baskets; the gas buret connected by means of a T-tube both with the source of hydrogen and with the absorption flask. Power is supplied by a $\frac{1}{2}$ horsepower motor belted to the camshaft. When in operation, the shaft has a speed of about 200 r.p.m. Hydro-

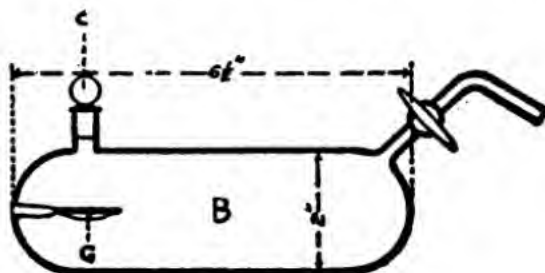


FIG. 29.

gen is supplied from a Kipp generator, or from a steel cylinder and is purified by being passed through a large wash bottle containing alkaline saturated permanganate and is washed with water at each gas buret by a separate wash bottle.

3219. Manipulation. The manipulation of a reduction is as follows: The air is first displaced from the entire apparatus by passing through it a current of hydrogen, after removing the stopper *C*, and lowering the reservoir *D*, so that sufficient water remains to form an air trap at the lower bend of the buret. The levels in both arms of the U-tube are then equalized

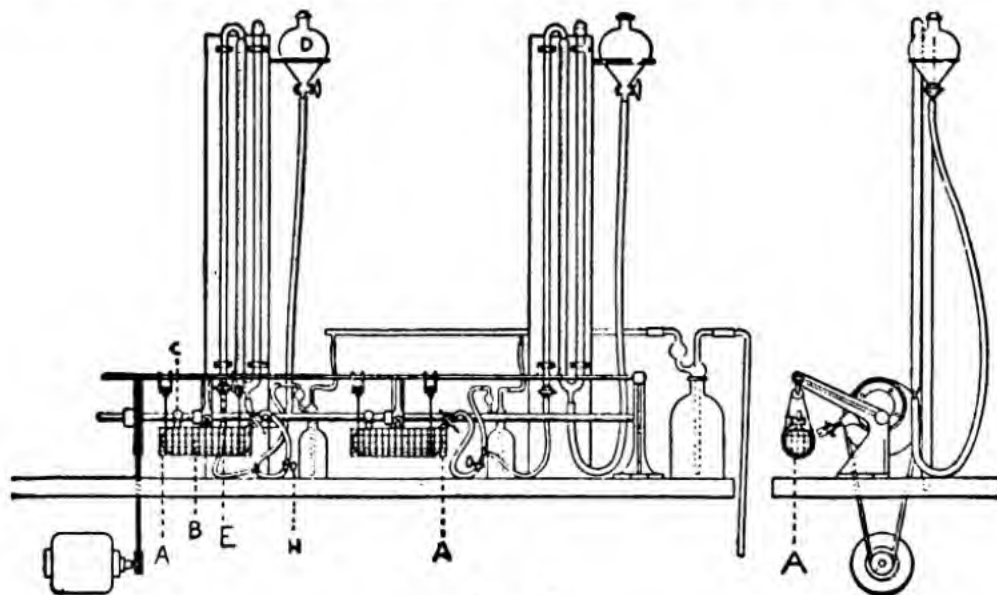


FIG. 30.

at the zero mark. The three-way stopcock *E*, is then closed, the stopper *C*, which had been replaced during the flushing of the buret with hydrogen, is removed, and 0.02 g. dry colloidal palladium introduced while a current of hydrogen is passing through. Then 50 cc. of 50 per cent alcohol are added, the stopper replaced, the stopcock closed, the three-way cock *E* momentarily opened to the air to equalize the pressure in the apparatus with that of the atmosphere, and the flask shaken until no more hydrogen is absorbed. In this way the errors due

to (1) absorption of hydrogen by the catalyzer, (2) solubility of the gas in the solvent, and (3) consumption of hydrogen by oxygen dissolved in the solvent, are removed from consideration. The buret is again filled to the zero mark with hydrogen and the shaking flask tilted until the palladium solution has drained from the concave "substance table" *G*. The substance under investigation is dropped into this table from an oil pipet (weighing bottle), again preventing the entrance of air by maintaining a current of hydrogen through the apparatus. The purpose of this "substance table" is to prevent contact between the catalyzer and substance under examination until the operator is ready to start the experiment. The stopper *C* is replaced, the cock is closed and the cock *E* opened momentarily to the air again. Connection is then made by the same stopcock between the shaking flask and the buret and the machine is at once set in motion. The absorption of hydrogen is carefully watched, maintaining the same water level in each side of the buret by regulating the flow of water from the reservoir. When the reaction is finished, a decided and abrupt decrease in the rate of absorption occurs. On the accuracy of the observation of this point depends the accuracy of the determination. The end-point may readily be found otherwise by noting the buret reading at frequent intervals, e.g., every fifteen seconds, and plotting volume against time on coordinate paper, when the break in the resulting curve will give the desired result. This point was found by drawing a straight line through the first points, then connecting with a smooth curve those points which lie at the right. The juncture of the straight line representing the main reaction, with the curved line representing absorption of hydrogen by secondary substances, if taken as the end-point.

3220. A method of determining the hydrogen value has been described by Waterman, Perquin and van Westen¹² which is said to permit of high precision. It is applicable even to substances having a high vapor pressure. Error due to occlusion of gases by the catalyst has been eliminated or reduced to a negligible minimum. The presence of oxygen in the hydrogen has also been prevented.

3221. The method for the determination of the hydrogen value mentioned in the foregoing paragraph has been applied to elaidic, linoleic and stearolic acids. The observations with elaidic acid are considered as standard measurements. It has been shown that $\Delta_{9,12}$ linoleic acid contains 2 double linkings. This fact proves that the abnormal behavior of thiocyanogen toward linoleic acid cannot be explained by the hypothesis of a triple and a double linking in this acid. The linoleic acid and the stearolic acid both consumed the theoretical quantity of hydrogen, viz., 2 mols of hydrogen per mol of the unsaturated fatty acid. The hydrogenation product in each of the 3 determinations was pure stearic acid.¹³

3222. Thiocyanogen Number. The mention in paragraph 3221 of the behavior of linoleic acid with thiocyanogen is a reference to results reported by Kaufmann.¹⁴ Kaufmann has introduced the "thiocyanogen number" as a chemical constant of unsaturated compounds and has applied it extensively to unsaturated fatty acids and their glycerides.¹⁵

3223. Thiocyanogen can be obtained free in solution by treating lead thiocyanate with bromine in presence of a suitable solvent, or by acting on a solution of lead tetra-acetate in glacial acetic acid with thiocyanic acid in excess of the quantity required by the equation: $\text{Pb}(\text{O}_2\text{C}\cdot\text{CH}_3)_4 + 4\text{HCNS} = \text{Pb}(\text{CNS})_2$

¹² *J.S.C.I.*, 1928, **47**, 363T.

¹³ Waterman, Bertram and van Westen. *J.S.C.I.*, 1929, **48**, 50T; *C. L.*, 1929, **23**, 2311.

¹⁴ *Arch. Pharm.*, 1925, **263**, 675; *Brit. Chem. Abst.*, 1926, 165B. See para. 3226.

¹⁵ Kaufmann and Gaertner, *Ber.*, 1924, **57B**, 928; *J. Chem. Soc. Abst.*, 1924, i, 840 (titration method); Kaufmann, *Ber.*, 1926, **59B**, 1390; *C. A.*, 1926, **20**, 2989 (application to tung oil).

+ (SCN)₂ + 4CH₃·CO₂H. In the latter case lead thiocyanate is precipitated and thiocyanogen remains in solution.

3224. For the preparation of volumetric solutions of thiocyanogen preferably anhydrous acetic acid is used because it affords the most stable solutions. Carbon disulphide, chloroform, ether, methyl alcohol and other solvents, though chemically saturated, form solutions of thiocyanogen which rapidly lose their strength.

3225. The thiocyanogen number, sometimes called the "rhodanometric" number, is expressed in terms of the iodine value. The usual titer of the solutions used is 0.05*N* or 0.1*N*. An excess of thiocyanogen (100–150 per cent) is used. After the reaction the excess is determined by agitation with twice the estimated quantity of potassium iodide, dissolved in water, and titrating the liberated iodine. Alcoholic sodium iodide solution may be used where the end-point is obscured by the presence of thiocyno compounds.

3226. A series of such rhodanometric determinations has been made on fats and oils. The results are expressed as if iodine had been used. In the list *R* denotes the thiocyanogen number, *I*, the (determined) iodine number (Hanus). The period of interaction is given.

Oil	Reaction Period	R	I
Castor.....	6–12 hours	81.6	82.6
Olive.....	5 hours	76.6	80.8
Peanut.....	12–15 hours	72.2	88.1 *
Almond.....	14 hours	84.5	97.7 †
Rape.....	5 hours	77.4	105.9
Sesame.....	7 hours	75.5	108.9
Linoleic glyceryl ester.....		82.5	169. ‡

* Mean of three.

† Mean of two.

‡ Cf., para. 3221.

3227. With purified fatty acids the following results were obtained.

Fatty acid	R	I
Oleic.....	90.6	90.6
Elaidic.....	81.5	81.6
Erucic.....	73.7	74
Brassicidic.....	73.2	73.8

EXPERIMENTAL RESEARCHES

SYNTHETIC ESTERS OF OLEIC AND OTHER FATTY ACIDS AND THEIR HYDROGENATED PRODUCTS

3228. In 1906 Bedford¹⁶ studied the esterification of linolic and linolenic acid and the hydrogenation of these esters in the presence of finely divided nickel.

3229. Methyl esters derived from thickened linseed oil were hydrogenated by Morrell,¹⁷ who employed colloidal palladium as a catalyzer. Stearic acid in good yield was obtained from the products of hydrogenation.

3230. The methyl, ethyl, propyl, isobutyl, amyl, benzyl, and glyceryl esters of oleic acid were prepared in the author's laboratory.¹⁸ They were all liquid at the ordinary temperature and yielded practically saturated products when hydrogenated in the liquid state, at an increased temperature, in presence of reduced nickel. The nature of the alcohol did not seem to have much effect on the rate or degree of hydrogenation. A product derived by heating oleic acid and aniline was found to hydrogenate readily to form a very hard product.

3231. Hydrogenation of Methyl Oleate. A portion of methyl oleate containing 1 per cent of finely divided metallic nickel (reduced for fifteen to twenty minutes in a stream of hydrogen at 320° to 350° C.) was treated for about two hours at about 180° to 200° C. with hydrogen which was simply allowed to bubble through the liquid as a brisk stream, thereby maintaining the catalyzer in suspension. The solid product obtained after filtration was white and crystalline. It had an iodine number of 0.4 and melted at 37° C.

3232. Ethyl Oleate. Ethyl oleate containing 1 per cent of metallic nickel (reduced for fifteen minutes in a stream of hydrogen at 320° to 350° C.) was exposed to a rapid current of hydrogen for about two hours. The oil was filtered through an ordinary filter paper in the hot oven. The product melted at 31° C. Its iodine number was 5.3.

3233. Propyl Oleate. The hydrogenation in this case was carried out under conditions practically identical with those employed in the hydrogenation of methyl and ethyl oleate. The hardened oil had an iodine number of 1.3. It melted at 27° C.

3234. Isobutyl Oleate. The ester was hydrogenated for about two hours in the presence of 1 per cent metallic nickel (reduced for fifteen minutes at 320° to 350° C.). The temperature of hydrogenation was 180° to 200° C. The hydrogenated product was soft and translucent and distinctly crystalline. It somewhat resembles crude paraffin. It had an iodine value of 0.2 and melted at 25° C.

3235. Amyl Oleate. This ester was hydrogenated under conditions similar to those employed above. The hydrogenated product was soft and non-homogeneous, consisting of a liquid oil and a crystalline body. It had an iodine value of 1.7 and melted at 22° C.

3236. Glyceryl Oleate. Oleic acid (56.4 g.) and 18.4 g. glycerine were heated for five hours at 240° C. with continuous stirring. The oily product was washed several times with warm water and dried. Its acid number was 0.6. In cool weather a crystalline body formed which rendered the ester opaque. The iodine number of the product was 69.4. Pure glycerol mono-oleate has an iodine number of 71.3. The ester was hydrogenated in the usual way. Treatment with hydrogen for about two hours at 180° to 200° C. gave a product which melted at 59° C. and possessed an iodine number of 6.5. The hydrogenated product was similar in appearance to a good grade of hardened cottonseed oil, except that it was somewhat darker in color.

3237. Benzyl Oleate. Hydrogenation in the presence of finely divided reduced nickel gave a product which had an iodine value of 6.3 and a melting-point of 28° C.

3238. Oleic Acid and Aniline. Aniline (24.4 g.) and 37 g. oleic acid were heated under a reflux condenser for four hours at 170° to 190° C. The mixture darkened considerably. It

¹⁶ Über die Ungesättigten Säuren des Leinöls," Dissertation, Erlangen, 1906; *Ber.*, 42, 1909, 1324.

¹⁷ *J.S.C.I.*, 1915, 107.

¹⁸ *J. Ind. Eng. Chem.*, 1916, 1105; *J.S.C.I.*, 1917, 39; *Chem. Abst.*, 1917, 218. See also U. S. Pat. 1,227,708, Sept. 3, 1928.

was steam-distilled until the distillate was free from aniline. The acid number of the steam-distilled product was 30.5. It became solid on standing. The substance was treated with a solution of sodium hydroxide and washed free from alkali and sodium oleate. The acid number of the product was reduced to 3.6. The product melted at 34° C. It was dark brown in color and had a greasy feel. The material was hydrogenated for two hours at 190° to 200° C. in the presence of 1 per cent finely divided reduced metallic nickel. The hydrogenated product was filtered in the hot oven. It had an iodine number of 30.5. The iodine value of the unhydrogenated substance was 69.5. The iodine value of oleic anilide is 71.6. The product melted at 76° C. and was very hard and brittle.

3239. A tabulation of these results follows.

Ester	Acid Number	Iodine Value	Hydrogenation Product	
			M.p. ° C.	Iodine Value
Methyl oleate.....	1.3	87.0	37	0.4
Ethyl oleate.....	0.6	83.3	31	5.3
Propyl oleate.....	0.5	77.9	27	1.3
Isobutyl oleate.....	0.4	75.7	25	0.2
Amyl oleate.....	0.7	71.3	22	1.7
Benzyl oleate.....	0.7	62.3	28	6.3
Glycerol mono-oleate.....	0.6	69.4	59	6.5
(Aniline compound).....	3.6	69.5	76	30.5

3240. Methyl Oleate, Erucate, Cetoleate and Clupanodonate. Ueno and Kuzei have timed the hydrogenation of these esters of acids of different degrees of unsaturation: The ester (0.5 g.) was hydrogenated in solution in glacial acetic acid or ethyl alcohol in the presence of platinum-black. Methyl oleate and erucate were found to require nearly equal lengths of time for complete hydrogenation; methyl erucate and cetoleate required less time than methyl clupanodonate. It is concluded that the length of time required for the complete hydrogenation is nearly equal for all those members of normal unsaturated acids that belong to the same series and have nearly equal molecular weight, but for acids of different degree of unsaturation the time required depends entirely on the degree of unsaturation, being longer as the acid is more unsaturated.¹⁹

3241. In hydrogenating the methyl esters of highly unsaturated acids from sardine oil, Toyama and Tsuchiga^{19a} found a difference in the course of the reaction depending on the nature of the catalyst. With a platinum-black catalyst solid fatty acids commenced to be formed from the beginning of the hydrogenation; with nickel, the highly unsaturated acids were reduced to the oleic acid stage before any solid acids appeared. It is to be noted that the work with platinum was done at room temperature.

3242. Hydrogenation of Methyl Palmitoleate. The proof that the palmitoleic acid of whale oil is derived from ordinary palmitic acid (*n*-hexadecic acid) was furnished by the hydrogenation of 67 g. of the pure methyl ester (i.e., 0.25 molecule) in the presence of reduced nickel at 170° C. The acid produced by hydrolysis of the distilled ester was crystallized from 85 per cent alcohol, when it melted at 62.5°. This melting-point was unchanged when the acid was mixed with an equal weight of pure palmitic acid. There is, therefore, no doubt that the palmitoleic acid of whale oil is a hexadecenoic acid, containing no branched chain of carbon atoms. (Armstrong and Hilditch, *J. Soc. Chem. Ind.*, 1925, **44**, 185T).

¹⁹ *J. Soc. Chem. Ind. (Japan)*, 1927, **30**, 268; *Brit. Chem. Abst.*, **1928**, 272A.

^{19a} *Chem. Umschau*, 1929, **36**, 49; *Chem. Abst.*, 1929, **23**, 2586.

HYDROGENATION OF GLYCERIDES

3243. Hydrogenation of Fatty Oils with Palladium Catalysts. Nord (*Z. angew. Chem.*, 1919, **32**, 305; *J.*, 1919, 913A) studied the hydrogenation of oils using palladium from palladium chloride as a catalyst. In view of the high cost of palladium this method is not likely to supersede the common one employing nickel. The only advantages it offers are that hydrogenation takes place more rapidly and at a much lower temperature. Nord states that when castor oil is hydrogenated by this method the hydroxyl groups are split up, whereas the results of others, using nickel as a catalyst, indicate a temperature of 200° is necessary before the hydroxyl group is affected.¹⁰ In using colloidal palladium it is necessary either to employ a solvent or to emulsify the oil with such an agent as gum arabic. Gum tragacanth is less suitable.¹¹

3244. Completely hydrogenated fats have been prepared by Mannich and Thiele¹² by the aid of a charcoal-palladium catalyzer carrying 2 per cent palladium in a container surrounded by an asbestos jacket and maintained at 100°. The catalytic material is subsequently and completely removed by filtration, yielding a product free from all contamination, an advantage stated to be not possessed by the colloidal reduction process. This method can with equal facility be carried out in a solvent medium. The oils operated upon and the constants of the resulting fats are given below:

Oils	Melting-point	Iodine No.	Saponification Number	Melting-point of Insoluble Fatty Acids (Hehner)
Olive.....	70°	0.2	190.9	71.0°
Almond.....	72°	0.0	191.8	71.0°
Peanut.....	64°-64.5°	0.0	191.6	67.0°
Sesame.....	68.5°	0.7	190.6	69.5°
Cacao butter.....	63.5°-64°	0.0	193.9	65.5°
Poppy.....	70.5°	0.3	191.3	71.0°
Linseed.....	68°	0.2	189.6	70.5°
Tallow.....	62°	0.1	197.7	64.0°
Lard.....	64°	1.0	196.8	62.0°
Cod liver.....	63°	1.2	186.2	59.0°

A chloroform solution of the hydrogenated cod-liver oil gave no coloration with sulphuric acid: this is not, however, a necessary result of complete hydrogenation of cod-liver oil.

3245. A thorough study of the results of partial hydrogenation of cottonseed oil has been made by Moore, Richter, and Van Arsdell.¹³ They state that inves-

¹⁰ Quoted from *Applied Chem. Rep. S.C.I.*, 1919, **4**, 298.

¹¹ Funk and Dubin, U. S. Pat. 1,649,520, 1927, use this method for cod-liver oil. See also: Abstracts in *Chem. Abst.* 1920, **14**, 853; *Chem. Ind.*, 1919, 913A, and comments by Skita, *Z. angew. Chem.* 1920, **33**, Au satzteil, 72, *Chem. Abst.*, 1921, **15**, 2734.

¹² *Ber. pharm. Ges.*, 1916, **26**, 36; *Chem. Abst.*, 1916, 2158; *J.S.C.I.*, 1916, 548.

¹³ *J. Ind. Eng. Chem.*, 1917, 451.

tigations heretofore have considered the unsaturated components as a whole, rather than as individual units and that they have studied the physical and chemical changes which take place in oil during the process of hydrogenation, particularly changes in the amount and character of the various fatty glycerides, and the effect of variable factors, such as temperature and pressure.

I. HYDROGENATION CURVES

3246. For the study of the glyceride changes during hydrogenation, the tests made on samples included iodine number and iodine number of liquid fatty acids, calculation giving the "component glycerides" (olein, linolin and saturated glycerides) of each sample. The smooth curves drawn through the points plotted on triangular diagrams always, in the cases studied, had the same general shape, suggestive of the hyperbola, concave toward the right-hand side of the triangle. The linolin is always found to decrease from that present in the original oil and the saturated glycerides always increase, while the olein rises to a maximum and then falls continuously. These changes are what would be expected, since hydrogenation must cause linolin to disappear, forming olein, while olein, hydrogenating more slowly, would at first increase and then eventually disappear, forming stearin, a saturated glyceride. The shape of the curve depends upon the relative velocity of these two actions, and it appears that this relative velocity must be subject to important variation, according to the experimental conditions.

3247. Effect of Temperature. The result obtained in Fig. 31 may be interpreted as follows: while both linolin and olein were hydrogenated faster at the high temperature than

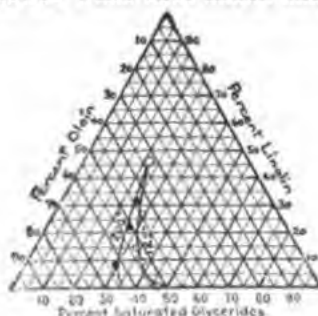


FIG. 31.—RUNS A AND B.

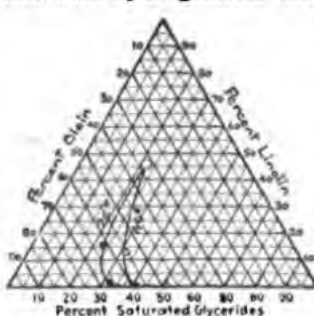


FIG. 32.—RUNS C AND D.

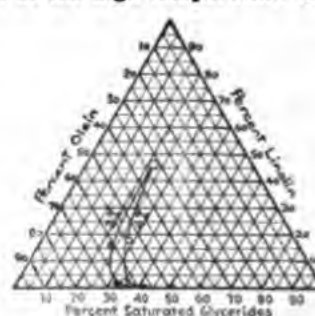


FIG. 33.—RUNS C AND E.

at the low temperature, relatively linolin was hydrogenated much faster at the high temperature, so that the olein had a greater tendency to accumulate under the latter conditions. In other words, both unsaturated radicals are acted upon in both cases, but at the higher temperature the more highly unsaturated one comes nearer to being *single out* for hydrogenation than at the lower temperature—the action is more "selective." This would be the case if, for instance, the temperature coefficient of the reaction linolin-olein is greater than that of the reaction olein-stearin, but in view of the complicated nature of the glycerides which are actually present that explanation is doubtless too superficial to be the entire truth.

3248. Effect of Pressure. The influence of the hydrogen pressure upon the course of the hydrogenation may be illustrated by Runs C and D (Fig. 32).

Increasing the pressure is here seen to have the opposite effect to increasing the temperature, so that at a high pressure the action is less "selective" than at a low pressure. An obvious corollary of this conclusion is that it would appear to be possible to duplicate at high pressure and high temperature a curve obtained at low pressure and low temperature, while the reaction as a whole might be made to proceed many times as fast in the former experiment as in the latter.

3249. In this case again a tentative "mechanism" may be put forward. It should first be noted that the occasional hydrogenation of a linolin chain clear to stearin instead of only to olein would have the same apparent effect as would an increase in the relative velocity of the olein-stearin reaction. Now if an increase in hydrogen concentration at the catalyzing surface (such as would be produced by increased pressure) caused an increase in the number of linolin chains to which 4 atoms of hydrogen were added at once, the observed effect would follow.

3350. TABLE OF TESTS FOR HYDROGENATION CURVES, EMPLOYING COTTONSEED OIL
 Abbreviations: LFA, Liquid Fatty Acids; SG, Saturated Glycerides; Ol, Olein; Lin., Linolin

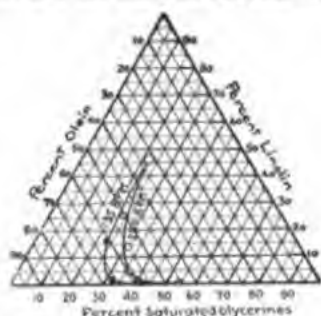
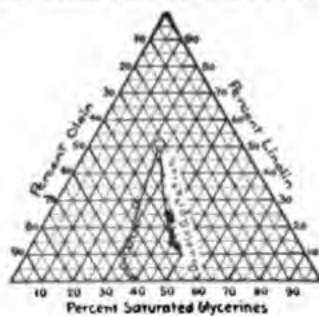
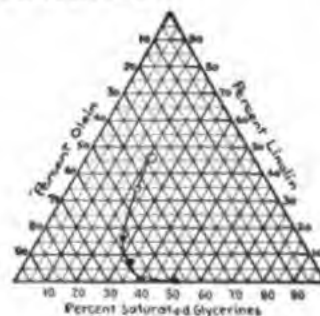
Experimental Conditions During Runs										Sam- ple	Iodine No.				Percentages				Iodine No.				Percentages			
Appa- ratus	Run	Temp.	Pressure	Catalyzer	Agitation	Oil Used	Sam- ple	Iodine No.				Percentages				Fat	LFA.	SG.	Ol.	Lin.	Fat	LFA.	SG.	Ol.	Lin.	
								Fat	LFA.		SG.	Ol.	Lin.													
Glass	A	125°	Atmos.	5% No. 1	Bubbling	A0	107.8	143.9	21.7	32.3	46.0	B0	107.8	143.9	21.7	32.3	46.0								
	B	200°	Atmos.	2% No. 1	Bubbling	1	84.5	124.6	29.0	44.2	26.8	1	92.8	128.2	24.4	43.9	31.7								
							2	70.5	110.2	33.1	52.2	14.7	2	82.3	117.9	27.0	50.8	22.2								
							3	61.9	103.4	37.5	53.1	9.4	3	68.5	101.1	29.2	62.2	8.6								
Iron	C	155°	20 lb.	2% No. 1	135 R.P.M.	C0	45.8	87.7	46.9	53.1	...	D0	107.7	143.9	21.7	32.3	46.0								
	D	155°	40 lb.	2% No. 1	135 R.P.M.	1	79.7	108.7	23.4	60.7	15.9	1	70.2	107.6	31.7	55.0	13.3								
							2	59.8	92.3	32.4	65.9	1.7	2	52.8	91.0	39.4	59.9	0.7								
							3	50.3	88.0	41.6	58.4	...	3	42.2	87.1	51.0	49.0	...								
Iron	E	155°	20 lb.	4% No. 1	135 R.P.M.	E0	107.7	143.9	21.7	32.3	46.0	F0	107.7	143.9	21.7	32.3	46.0								
	F	155°	20 lb.	2% No. 1	250 R.P.M.	1	77.2	112.0	27.9	54.4	17.7	1	87.3	120.4	24.3	50.4	25.3								
							2	57.6	92.4	34.8	63.3	1.9	2	71.5	108.5	31.1	54.9	14.0								
							3	42.9	86.4	50.3	49.7	...	3	59.7	97.1	35.7	59.3	5.0								
Glass	G	160°	Atmos.	No. 2	Bubbling	G0	110.9	149.1	22.4	27.2	50.4	H0	110.9	149.1	22.4	27.2	50.4								
	H	160°	Atmos.	No. 2	Grate doubled	1	88.4	125.1	26.2	45.3	28.5	1	74.9	126.9	38.4	36.6	25.0								
							2	79.6	118.5	29.8	48.2	22.0	2	71.5	124.9	40.1	37.0	22.9								
							3	75.0	113.3	30.8	51.4	17.8	3	66.8	119.3	41.6	39.5	18.9								
Iron	I	155°	40 lb.	2% No. 1	135 R.P.M.	10 lb.	4	71.7	108.8	31.0	54.9	14.1	4	63.5	117.1	43.4	39.8	16.8								
	J	155°	40 lb.	2% No. 1	135 R.P.M.	20 lb.	5	68.8	104.7	31.3	57.7	11.0	5	60.6	114.2	44.6	40.6	14.8								
							6	61.6	97.1	33.8	60.9	5.3	6	57.2	112.6	46.9	40.0	13.1								
							7	52.2	90.5	39.7	60.0	0.3	J0	108.4	142.8	20.6	33.5	45.9								
Iron		155°	40 lb.	2% No. 1	135 R.P.M.		10	108.4	142.8	20.6	33.5	45.9														
		155°	40 lb.	2% No. 1	135 R.P.M.		1	97.4	130.6	22.1	43.4	34.5	1	77.1	110.5	27.0	56.6	16.4								
							2	78.9	112.6	26.8	55.1	18.1	2	63.7	100.4	33.6	58.9	7.5								
							3	66.8	101.3	31.2	60.3	8.5	3	42.1	87.5	51.1	48.9	...								
							4	51.0	91.6	41.8	73.3	.09														

Catalyzer No. 1, Green nickel oxide reduced in hydrogen four hours at 320°-340° C., pressure 30-60 lbs. Catalyzer No. 2, Basic nickel carbonate and infusorial earth, calcined and reduced in hydrogen at 400°-500° C., four to fourteen hours, at atmospheric pressure.

3251. Influence of Percentage of Catalyst. The influence of percentage of catalyst was illustrated in Experiments *C* and *E* (Fig. 33). In this case the observed result, which shows a divergence in the same direction for increased percentage of catalyst as for increased pressure, seems to be at variance with what is commonly understood to be a law of catalytic reactions, namely that if the amount (or surface) of the catalyst be increased, all of the reactions involved will be speeded up by exactly proportional amounts. In this case, one reaction (olein-stearin) appears to be accelerated more than the other. The scheme advanced in the preceding section may be made to give a satisfactory explanation; in that section the concentration of hydrogen at the catalyzing surface was taken to be the controlling factor. Now increasing the percentage of catalyst must increase this concentration, for the average distance between a catalyst particle and the hydrogen bubble-surfaces is made smaller, thereby decreasing the lag between the "demand" for hydrogen at the catalyst surface, and the "supply," which must be kept up by the processes of solution and diffusion. Thus an increase in percentage of catalyst would cause an increase in the formation of stearin relative to the change in linolin, as in the two curves reproduced above.

3252. Effect of Agitation. The influence of degree of agitation on the path of hydrogenation was determined first by comparing Experiments *C* and *F* (Fig. 34), in which an iron apparatus with mechanical agitator was used. "Degree of Agitation" is a magnitude which is not easily expressed in quantitative form, but the revolutions per minute of an agitating device may serve as an index of the agitation, as least for moderate speeds.

3253. Another pair of experiments carried out in the glass flask, bubbling hydrogen, conditions were identical in both experiments except that in Run *H*, the hydrogen was bubbled through the flask at approximately twice the rate used in Run *G* (Fig. 35).

FIG. 34.—RUNS *C* AND *F*.FIG. 35.—RUNS *G* AND *H*.FIG. 36.—RUNS *I* AND *J*.

3254. In both pairs of experiments the influence of increased agitation is shown to be the same as that of increased pressure or per cent catalyst, and in the case of Runs *G* and *H* the variation in the curves is striking. The effect of doubling the volume of gas supplied, when the bubbling is already vigorous, may well be to increase the true "agitation" many times. On the other hand, doubling the revolutions per minute of a mechanical agitator possibly does not even double the agitation, since at high speeds there is a strong tendency for the whole body of oil to rotate without much disturbance.

3255. It may readily be seen that the "mechanism" suggested in the preceding section applies to the present case just as well, since the effect of increasing the agitation is to increase the number and surface of hydrogen bubbles and also to decrease their average distance from catalyst particles.

3256. Size of Apparatus. The size of the apparatus in which the hydrogenation is carried out apparently does not affect the path of the hydrogenation as appears from the data of Runs *I* and *J* (Fig. 36). It is of course, not certain that 135 r.p.m. produces the same "degree of agitation" in both cases; if the agitation is really better at this speed in the large machine, the effect of the increase in size on the path of hydrogenation is in the opposite direction to the effect of increased agitation.

3257. Influence of Material of Catalyst. When some other catalyst than nickel is used as in Experiment *K*, in which 1 per cent palladium (in PdCl_2 , method of Paal patent ^{23a}) acted as catalyst, the hydrogenation curve is found to have the same general characteristics as

^{23a} Carl Paal, U. S. Pat. 1,023,753, April 16, 1912. An equivalent amount of solid Na_2CO_3 is used as a neutralizing agent.

those described before. Bubbling apparatus was used, a temperature of 135° C. and atmospheric pressure. No experiment using nickel catalyzer is available to compare directly with it.

EXPERIMENT WITH PALLADIUM AS CATALYZER

Run Sample	Iodine Number		Percentages Calculated		
	Fat	Liquid Fatty Acid	Saturated Glycerides	Olein	Linolin
Ko	108.4	142.8	20.6	33.5	45.9
1	89.1	125.0	25.5	46.0	28.5
2	76.6	113.1	29.2	52.8	18.0
3	64.5	97.1	30.6	63.8	5.6
4	53.0	90.3	38.6	61.3	0.1

3258. Summary of Hydrogenation Curves. To summarize the conclusions from the preceding experiments, it appears that the chemical character of a partially hydrogenated oil is determined by the conditions of the hydrogenation. Thus to obtain a product of the same iodine number as another but relatively higher in saturated glycerides and linolin, the operating conditions should compare as follows with those in the other case: temperature lower, pressure higher, agitation more violent and percentage catalyzer greater. It is interesting to note that it is possible to hydrogenate the linolin to olein with only the slightest increase in saturated glycerides by operating at a high temperature, low pressure and low agitation, and using only a small amount of catalyzer.

II. CHANGES IN CHEMICAL CONSTANTS OF OIL DURING HYDROGENATION

3259. Of all the "chemical constants" of cottonseed oil, the iodine number (with its variations, the "hydrogen number," Mauméné number and heat of bromination), is the only one which is changed markedly by hydrogenation. Saponification value, acetyl value, Reichert-Meissel number and percentage of free fatty acids change either not at all, or only slightly.

3260. The drop in iodine number, however, is one of the most striking effects of hydrogenation, and it has been commonly used in the past to indicate the progress of the reaction.²⁴ Fokin concludes, from a study of the hydrogen absorption, that "the reduction procedure is included in the category of monomolecular reactions," but notices that the curves "often show a straightening out toward the abscissa axis." He comes to the conclusion that the conditions which determine the shape of the curve are: (a) the velocity of diffusion of the gas (presumably through the oil); (b) the condition of the catalyzing surface; and (c) the presence of catalyzer poisons. Very similar conclusions were published by Böeseken,^{24a} but most of his work was on organic compounds of lower molecular weight than the oils.

3261. Pressure. Early investigators appreciated the fact that the hydrogenation reaction is accelerated by pressure, and Moore, Richter and Van Arsdell state that, so far as is known, all of the commercial oil-hardening processes are carried out at gas pressures ranging from 20 to 150 lb. or even higher. Comparison of the two curves of Fig. 37 shows that the time required to reduce the iodine number of the oil to any specified figure is roughly cut in half by doubling the pressure, i.e., in these experiments the rate of hydrogenation was approximately proportional to the hydrogen pressure.

3262. Temperature. It is likewise well known that the hydrogenation reactions in oil have a positive temperature coefficient, i.e., the rate is greater the higher the temperature, although the thermal decomposition of the oil sets an upper limit to the available range at about 250° C. The hydrogenation reactions in oil have a positive temperature coefficient in the range between

²⁴ Paal-Roth, *Ber.*, **41**, 2282-2291; Fokin, *Z. angew. Chem.*, **22**, 1451-1459, 1492-1502; Bömer, *Z. Nahr. Genussm.*, **24**, 104-113. Paal and his co-workers, and Fokin recorded the volume of hydrogen absorbed at various stages of the process, thereby determining directly the amount of saturation which had taken place, instead of indirectly by means of the iodine number.

^{24a} *Rec. trav. chim.*, 1916, **35**, 260-287.

35° and somewhat above 200° C.—possibly up to 240° C., but as may be seen from a study of the curves of Fig. 37a, this coefficient drops consistently as the temperature rises. Thus for the range of temperatures 35° to 125° the time required to reach a certain iodine number is on the average decreased about 35 per cent for each 10° rise in temperature, while for the range 160° to 200° this coefficient is less than 20 per cent. Since the commercial processes nearly all operate at temperatures of 160° to 180°, it is evident that no material gain in time could be made by the use of higher temperatures, and the point of maximum economy is probably being realized.

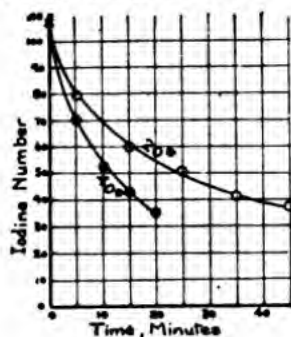


FIG. 37.

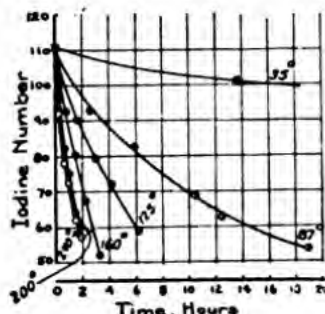


FIG. 37a.

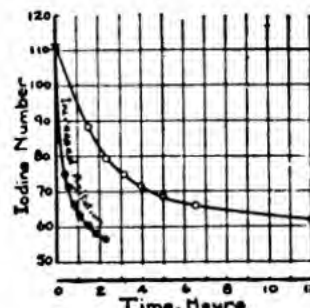


FIG. 37b.

3263. Agitation. The increase in velocity of reaction due to increased agitation of oil and catalyzer with hydrogen is shown in Fig. 37b. In this case an increase of about 100 per cent in the volume of hydrogen supplied increased the velocity of the reaction 800 to 1000 per cent. In apparatus of this type handling charges of commercial size it is not usual to cause such violent agitation as is easily brought about in a 2-liter flask, and it is doubtful whether doubling the hydrogen supply would, on a large scale, more than double the reaction-rate. The importance of efficient agitation, or of intimate commixture of the oil, catalyzer and hydrogen, has apparently been realized by nearly all of the workers in this field, as witness the patent files, but there is no observation recording such a great increase in agitation as the above, brought about by such simple means.

Catalyzer. As in practically all catalytic reactions, the speed of hydrogenation is increased as the percentage of catalyzer is raised. The time required to reach a given iodine number is roughly proportioned to the percentage of catalyzer (Fig. 38). Considerations of outlay required for catalyzer preparation and recovery limit the amount used in commercial batch processes, however, to 1, or at most, 2 per cent. When a very good grade of refined oil is used, as little as 0.1 per cent nickel is common practice, high pressure and agitation being relied upon to reduce the time consumed.

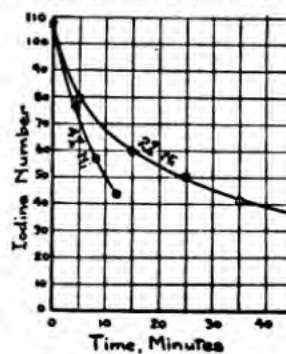


FIG. 38.

3264. Summary of Iodine Number-time Curves. To summarize, increasing the pressure, temperature, agitation or amount of catalyzer will increase the rate at which cottonseed oil is hydrogenated. This increase in rate is roughly proportional to the increase in pressure or amount of catalyzer, while raising the temperature 10° in the region of common practice, 160° to 180°, increases the rate only about 20 per cent. Increase in agitation (difficult to measure quantitatively) produces a marked increase in the reaction-rate.

III. CHANGES IN PHYSICAL CONSTANTS OF OIL DURING HYDROGENATION

3265. Melting-point. The most striking effect of the hydrogenation of an oil is, of course, the gradual increase in solidity, with the accompanying change in such physical constants as melting-point and titer. Oil was hydrogenated with mechanical agitation of 108 r.p.m., temperature 160° C., pressure 20 lb., catalyzer 5 per cent nickel on a carrier. The melting-point and iodine number were among the constants determined on each sample, and these constants compared as follows:

	M ₀	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆
Melting-point, °C.....	9.0	39.4	40.8	45.8	48.0	48.9	60.5
Iodine number.....	107	74.3	66.7	61.0	54.5	48.5	0.4

There can be no doubt that while the two ends of this curve remain fixed, the intermediate points are capable of considerable variation from the curve, depending on the conditions of hydrogenation. Note, for instance, the points *A* and *B* on Fig. 39. Sample *A* was made by one of the "continuous" processes from the same kind of cotton-oil, while Sample *B* was made at a very high temperature.

3266. Titer. The titer of an oil or fat, being the solidification-point of its fatty acids, might be expected to share the characteristic of the melting-point of the fat, namely, a gradual increase with hydrogenation. It is found, however, to show the peculiarity of first decreasing, passing through a minimum, and then increasing steadily. Cotton-oil was hydrogenated with 5 per cent of nickel, on a carrier, in one case at 125° C., and in the other at 200° C. Titer and iodine number were among the determinations made on each sample. In Fig. 39a titer is plotted against time and in Fig. 39b against iodine number.

3267. The apparently anomalous fact that the addition of more saturated, higher melting acids at first lowers, instead of raising the solidification point is evidently due to the existence of a eutectic, or low melting mixture of the components. According as the path of hydrogenation carries the composition close to or far from this point the minimum attained will be lower or higher. From Fig. 39a it is evident that the low-temperature run passed closer to the

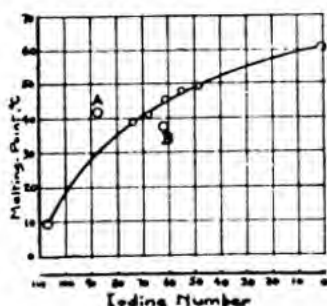


FIG. 39.

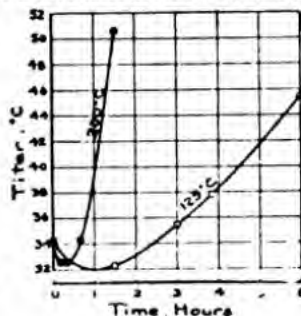


FIG. 39a.

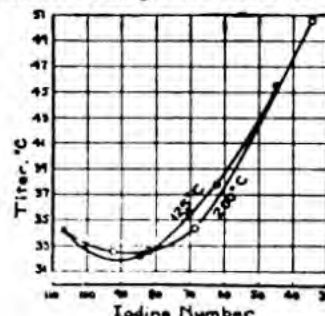


FIG. 39b.

eutectic point than did the high-temperature run. Below iodine number 50 the two runs were practically identical, as would be expected from the fact that since linolin has largely disappeared the two hydrogenation curves of component glycerides cannot differ very greatly.

3268. Commenting on the article by Moore, Richter and Van Arsdel, Lowenstein²⁵ expresses surprise that the writers of this article made the statement that the amount of hydrogenation which is required to render the oil just incapable of responding to the Halphen test has not to their knowledge been investigated, in view of Lowenstein's Patent No. 1,187,999. See paras. 3936-3939, page 446.

3269. Responding to this, Moore, Richter and Van Arsdel comment as follows: In reply to Dr. Arthur Lowenstein's criticism of a section in our article on "The Incomplete Hydrogenation of Cottonseed Oil," we wish to state that U. S. Pat. 1,187,999 was familiar to us at the time the section in question was written: neither at that time nor at the present time, however, could we regard the disclosures of the patent as constituting anticipation of our work.

3270. The fundamental statement of the patent, as quoted above by Dr. Lowenstein, is as follows: "... the hydrogenation process is continued until a sample of the oil fails to respond to the Halphen reaction and the desired degree of crystallization takes place when the oil is chilled. There is no warrant for assuming from the language of the patent that when the Halphen test is just destroyed the proper amount of crystallizable material has just been produced; in fact it would appear that a considerable degree of choice may be exercised in the production of this stearin after the Halphen test response is gone.

²⁵ *J. Ind. Eng. Chem.*, 9, 719.

3271. The iodine number of the product of the patent is not stated to be that of a product in which the response to Halphen test has just been destroyed, but is that of a product in which both conditions have been met. The breadth of the range given, 90 to 102, indicates that "the desired degree of crystallization" upon chilling is subject to considerable variation, according to the object in view.

3272. The other distinguishing mark given in the patent, namely, a range of increase in titer, likewise fails to disclose any definite knowledge of the degree of hydrogenation necessary to destroy the response to the test; its indication is ambiguous like that of the iodine number. We have not experimented with the Wolfbauer method, since its use is uncommon in this country, but it is certain that the range of 0.1° to 0.5° C. represents a very large range in actual hydrogenation, as measured by change in iodine number. It is noteworthy that our experiments invariably showed a decrease in titer, as measured by the A.O.A.C. method, before any increase began, so that to increase the titer 0.1° to 0.5° above that of the original oil required a drop of iodine number to about 70.

3273. We wish to point out that if, as Dr. Lowenstein asserts, there are "many variable factors which would have an effect on this conclusion," there exists no published evidence to that effect. It seems probable to us that temperature is the only factor which would have such an effect, and the temperature 150° to 160° C. was specified in the experiment in question.

3274. We are, therefore, unable to agree with Dr. Lowenstein's implication that U. S. Pat. 1,187,999 anticipates our disclosure. It is quite possible that other investigators have carried out the same work at an earlier date, but we believe ourselves to have been the first to publish the results of such work."

3275. The rate of hardening of cottonseed oil by nickel and "nickel oxide" catalyzers has been investigated by Meigen and Bartels (*J. prakt. Chem.*, 1914,

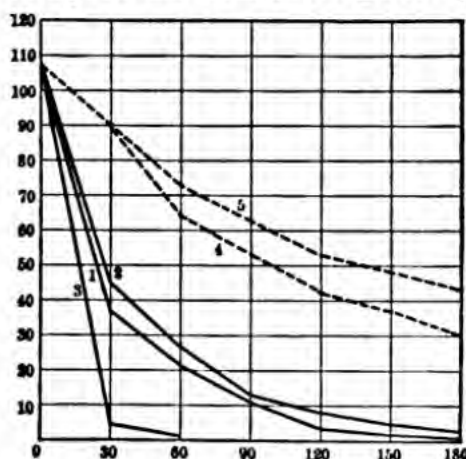


FIG. 40.

293) and their results are shown in Fig. 40. Curves 1, 2 and 3 were derived with metallic nickel at 170° C., and 4 and 5 with nickel oxide at 250° to 255° C. The amount of catalyzer in all cases corresponded to 2 per cent of nickel oxide. No. 1 was obtained with nickel prepared from the carbonate, No. 2 from reduced oxide and No. 3 from a commercially used catalyzer. The oxide employed in Nos. 4 and 5 was obtained by ignition of the nitrate. These curves indicate a slower action for the oxide, which Meigen and Bartels attribute to the time required for preliminary reduction of the oxide

after its addition to the oil, and before actual hydrogenation of the oil occurs.

3276. Tsujimoto has prepared and examined hydrogenated chrysalis oil. He has found raw chrysalis oil to be unsuitable for the purpose of hydrogenation, as its nitrogenous and other impurities largely affect the activity of the catalyzer. The refining of chrysalis oil is by no means easy; but a method proposed by Tsujimoto, which essentially consists in heating the oil with 5 to 10 per cent by volume of dilute sulphuric acid (sp. gr. 1.39) followed by treatment with Kambara earth, gives an excellent result. The refined oil hardened by nickel catalyzer is a white fat which may be used as a raw material for soap making.

3277. Tsujimoto has noted that the fatty acids of chrysalis oil consist of about 25 per cent saturated and 75 per cent unsaturated acids (iodine value 178.73). Among the saturated

acids, palmitic acid was identified; stearic acid is probably not present. The unsaturated acids consist of oleic, linolenic and isolinolenic acids; besides them, some isomers of linolic acid are present in a larger quantity.

3278. If the conclusions reached in the above-mentioned investigation be correct, the final product of the hydrogenation of these unsaturated acids must be stearic acid. Tsujimoto considered that a study of the product was important from the point of view of utilizing the hardened chrysalis oil for technical purposes and accordingly made certain experiments which are described in the following paragraph.

3279. Fifty grams of chrysalis oil were saponified in a flask with 38 cc. of 50 per cent aqueous solution of KOH and 133 cc. of 96 per cent alcohol, by warming on a water-bath; the excess of alkali was neutralized with acetic acid and 500 cc. of 7 per cent aqueous lead acetate solution was stirred into it. The resulting lead soap was twice washed with 500 cc. of hot water and treated with 500 cc. of ether at 10° C. and then filtered. (Tortelli and Ruggeri's method.) The filtrate was then treated with dilute HCl, in order to decompose the lead soap, and was well washed with water: 250 cc. of the ethereal solution of the free unsaturated acids thus obtained, which contain about 20 g. of acids of iodine value 176.17, were transferred into a strong glass bottle; 0.5 g. of Loew's platinum-black was added. The bottle was then connected to a hydrogen holder. On expelling the air from the bottle by hydrogen, it was strongly shaken by means of a mechanical contrivance. After three and one-half hours' shaking, a loss of about 2900 cc. of hydrogen was observed on the holder. Here the hydrogenation was stopped for a time. On evaporating off the ether, a residue amounting to 17.52 g. was obtained. It was a brown-yellow crystalline mass which, when melted, formed a brown-red liquid; it melted at 56.2° C., having the neutralization value 188.92 and iodine value 45.91. The hydrogenation was apparently incomplete; but before continuing the operation, it was found better to remove the unsaponifiable and coloring matter from the product. Eleven grams of the above product were saponified with 50 cc. of 8 per cent alcoholic solution of NaOH; then 5 g. of NaHCO₃ and about 50 g. of pure sand were thoroughly mixed with it. The mass was dried, powdered and exhausted in a Soxhlet extractor with petroleum ether. The crude unsaponifiable matter thus extracted was 2.22 per cent. The soap in the extractor was dissolved in hot water and decomposed with dilute HCl and then taken up with ether. The ethereal solution of the fatty acids which appeared brownish yellow, was decolorized with animal charcoal, and made up to 250 cc. by adding ether; then adding 0.3 g. of the platinum-black, it was hydrogenized for two hours in the same way as before (the reading of the volume of hydrogen was omitted.) On evaporating off the ether, 8.3 g. of the hydrogenated acids were obtained. The white crystalline mass had a melting-point of 68° to 68.5° C., neutralization value 195.19 and iodine value 0. This product is, therefore, a saturated compound, which in its melting-point and neutralization value nearly coincides with stearic acid (melting-point 69.3° C., neutralization value 197.5, molecular weight 284). A mixture of the product with about an equal quantity of pure stearic acid melted at 68° to 68.3° C. In order to perform the fractional crystallization of the acids, 5 g. of the hydrogenated product were dissolved in 100 cc. of 90 per cent alcohol and separated into three portions successively as follows: (1) 4.27 g.; white laminae with pearly luster; melting-point 69.5° to 70° C.; neutralization value 197.82; mean mol. wt. 283.59. A mixture with pure stearic acid melted at 69.5° to 69.7° C. (2) 0.21 g.; melting-point 68° C.; neutralization value 197.20. (3) Residue left on evaporating the mother liquor, 0.41 g.; a little colored solid; melting-point 50° C.; neutralization value 177.42. The low melting-point and neutralization value are probably due to the accumulation of the impurities in this part and also to the esterification of the acids on evaporating off alcohol. The result of the elementary analysis of (1) was as follows: 0.1245 gave 0.3487 CO₂ and 0.1439 H₂O; C = 76.39; H = 12.84. C₁₈H₃₆O₂ required C = 76.06; H = 12.68. Therefore the substance is stearic acid. From the above, it was concluded that the hydrogenated product of the unsaturated fatty acids of chrysalis oil consists mainly of stearic acid.²⁶

3280. Hydrogenation of Corn Oil. Reichert and Trelles,²⁷ using nickel or platinum catalyst studied the hydrogenation of corn oil. They say that: 1. The oil must be free from water. 2. Extraction naphtha may leave in the oil catalyst poisons. 3. The optimum temperature is 210°-230° C. 4. With nickel

²⁶ *Ind. Eng. Chem.*, 1916, 802.

²⁷ *Anal. Asoc. Quim. Argentina*, 1921, 9, 86; *J.S.C.I.*, Aug. 15, 1921, 551A.

catalyst after four hours the iodine value was 44.5, with platinum after three hours it was 21, and the product obtained which had m.p. 57° C.²⁸

3281. Glycerides of Erucic Acid. Sudborough, Watson and Ayyar²⁹ prepared behenic acid from various sources and found it had m.p. 79.3°–80° C. This valuable article reports elaborate analyses of oil containing glycerides of erucic acid, $\text{CH}_3 \cdot (\text{CH}_2)_7 \cdot \text{CH} = \text{CH} \cdot (\text{CH}_2)_{11} \cdot \text{COOH}$. Rape oil was found to contain a catalyst poison, probably a sulphur compound. This poison could be fixed by a preliminary treatment with nickel: on continuing the hydrogenation with a fresh batch of catalyst, the hardening progressed smoothly. A similar difficulty and remedy are noted by Sudborough *et al.*³⁰ in the case of the fat from *Salvadora oleoides* (Khakan fat).

3282. The hydrogenation process has been used by Twitchell for the preparation of saturated fatty acids in connection with a study of the melting- and solidifying-points of mixtures of fatty acids and the use of these points to determine the composition of such mixtures.³¹

A. Twitchell prepared three fatty acids, stearic, palmitic and behenic acid, in a fairly pure state.

B. The stearic acid was obtained from hydrogenated corn oil. The fatty acids from this were distilled in a current of superheated steam and the last fraction crystallized a number of times from petroleum ether and from alcohol. This stearic acid had a solidifying-point of 69.04 and a melting-point in a capillary tube of 69.30°. Its combining weight, by titration with alkali, was 284. It was not quite pure, as the last crystallization still caused a slight increase of the solidifying-point.

C. The palmitic acid was obtained from myrtle wax, the fatty acids of which were distilled and then crystallized several times from petroleum ether and then from alcohol. This had a solidifying-point of 62.14 and a melting-point of 62.44. Its combining weight was 255.3.

D. The behenic acid was obtained from hydrogenated menhaden oil, the fatty acids of which were distilled and the last fractions crystallized ten times alternately from petroleum ether and alcohol. It had a solidifying-point of 79.59° and a melting-point of 79.99°. Its combining weight was 340.9.

E. It can be assumed, Twitchell states, that on hydrogenating a fat, all those unsaturated acids containing 18 carbon atoms in the molecule are converted into stearic acid, all those containing 16 carbon atoms into palmitic acid and all those containing 22 carbon atoms into behenic acid. On comparing the mixtures obtained it is seen that the palmitic acid has not increased in the fatty acids of the hydrogenated product; therefore, cottonseed oil fatty acids contain no unsaturated acids with 16 carbon atoms. As the hydrogenated oil fatty acids contain 70.8 per cent stearic acid plus 2.0 per cent of oleic acid the original oil fatty acids would contain about 72.8 per cent of unsaturated acids with 18 carbon atoms, provided there was no stearic acid originally present; at any rate, it can be concluded that all the unsaturated acids of cottonseed oil have 18 carbon atoms in the molecule.

F. The composition of the fatty acids of cottonseed oil is therefore about as follows:

Palmitic acid	25.9 per cent
Unsaturated acids with 18 carbon atoms	72.8 per cent

G. The increase in weight due to addition of hydrogen, being very small, has not been considered in the above calculations.

H. The hydrogenated fatty acids were shown to contain 25.9 per cent of stearic, 23.2 per cent of palmitic acid and 18.7 per cent of behenic acid. The palmitic acid was present in the

²⁸ At the temperatures mentioned, with a nickel catalyst, it is conceivable that there is some tendency for dehydrogenation to take place, which may explain the remarkably high iodine number of the product.

²⁹ *J. Indian Inst. Sci.*, 1926, **9A**, 25; *Chem. Abst.*, 1927, 506; *J.S.C.I. Suppl.*, **B**, 1926, 954.

³⁰ *J. Indian Inst. Sci.*, 1926, **9A**, 117.

³¹ *J. Ind. Eng. Chem.*, 1914, 564.

original oil, but the stearic and behenic acids have been formed from unsaturated acids with 18 and 22 carbon atoms, respectively.

I. The results indicate a composition for menhaden oil fatty acids about as follows:

Palmitic acid	22.7
Other solid, saturated acids	11.8
Unsaturated acids with 16 carbon atoms	None
Unsaturated acids with 18 carbon atoms	26.7
Unsaturated acids with 22 carbon atoms	20.2
Other saturated acids	18.6
	<hr/>
	100.0

These fatty acids, therefore, probably contain about 18.6 per cent of another unsaturated acid with some other number of carbon atoms, and also 11.8 per cent of another saturated acid.

3283. In the course of Twitchell's work on menhaden oil as above outlined, a fractional distillation was made of a fatty acid separated from the hydrogenated oil. There were twenty-one fractions in all. In this distillate were found behenic, stearic and palmitic acid. The presence of arachidic and myristic acid seemed probable but having neither of these acids in the pure form, Twitchell could not at that time establish their presence in any of the fractions. He therefore carried out the following investigations:²²

3284. Myristic Acid. If any myristic acid were present it would very likely be found in the first fraction. To further concentrate it, a portion of this fraction was dissolved in alcohol, partially precipitated with lead acetate and filtered. The fatty acids were separated from the filtrate and melted in the proportion of 20 parts with 80 parts of myristic acid:

The melting-point of this mixture was	51.60°
That of pure of myristic acid is	53.76°
	<hr/>
The lowering of the melting-point was therefore	2.16°
The lowering of the melting-point of myristic acid by 20 per cent of palmitic acid is ..	4.53°
The percentage of myristic acid in the fatty acids under examination is therefore	
$100 \times (4.53 - 2.16)/4.53 =$	52.3%

which clearly establishes the presence of myristic acid in the hydrogenated oil.

3284A. Arachidic Acid in Hydrogenated Menhaden Oil. Fractions 15 and 16 of this same distillate had an average combining weight of 308.5 and were the most likely to contain arachidic acid. They were united and crystallized twice from 90 per cent alcohol at 15° C. The mean combining weight of the crystals was 324. In previous work it had been shown that behenic acid (molecular weight 340) was present in the hydrogenated oil. It would almost certainly be in this fraction. It remained to determine whether the reduction in combining weight was due to arachidic acid.

20 parts of the crystals melted with 80 parts of arachidic acid has a melting-point of ..	72.95°
Arachidic acid has a melting-point of	74.78°
	<hr/>
The lowering of the melting-point was therefore	1.83°
The lowering of the melting-point of arachidic acid by 20 per cent of behenic acid	3.61°
The percentage of arachidic acid in the crystals is therefore $100 \times (3.62 -$	
$1.83)/3.61 =$	49.3%

which establishes the presence of arachidic acid in the hydrogenated oil.

3285. General Results. Having found myristic acid in both the original and the hydrogenated fatty acids in equal amounts, it was not produced by hydrogenation. On the other hand arachidic acid was found only in the hydrogenated and not in the original fatty acids.

²² *J. Ind. Eng. Chem.*, 1917, 582.

It was therefore produced by the addition of hydrogen to an unsaturated acid with 20 atoms of carbon.

A. The composition of the menhaden oil fatty acid described in Twitchell's paper of July, 1914, can now be definitely stated as follows:

	Degrees
Palmitic acid.....	22.7
Myristic acid.....	9.2
Stearic acid.....	1.8
Unsaturated acids with 16 carbon atoms.....	None
Unsaturated acids with 18 carbon atoms = 26.7 less 1.8 per cent stearic acid =	24.9
Unsaturated acids with 20 carbon atoms.....	22.2
Unsaturated acids with 22 carbon atoms.....	20.2

B. From certain observations, Twitchell concludes that the unsaturated acid with 22 carbon atoms found in menhaden oil and which, like erucic acid, is converted by hydrogenation into behenic acid, is nevertheless not erucic acid, since on fusion with caustic potash it is not converted into arachidic acid. It is probably a more unsaturated acid which is converted into stearic or palmitic acid by the fusion.

3285A. A sample of butter fat examined by Amberger³³ contained only 2.4 per cent of triolein. By fractional crystallization of the glycerides of hydrogenated butter fat, it was found that the olein had not been converted into tristearin, but into a mixed glyceride. The greater part of the oleic acid in butter fat is therefore present as a mixed glyceride and not as triolein. Butyric and caproic acids are also present as mixed glycerides; tributyrin and tricaproin could not be isolated from the fat. Butyro-diolein, butyro-palmito-olein, and oleo-dipalmitin are present, as is shown by analysis of the glycerides isolated from the alcohol-soluble portion of hydrogenated butter fat. Amberger has also isolated another glyceride, m. p. 67.9 C., from butter fat; this glyceride yielded a mixture of fatty acids, m. p. 55.5° C.

3286. Hydrogenation of Vegetable Oils with Water-gas. Butkovskii³⁴ succeeded in hydrogenating, on a laboratory scale, a mixture of equal parts of sunflower and cottonseed oil, using specially purified water-gas and a nickel catalyst. The water-gas was passed through, successively, double normal NaOH, ferric oxide powder mixed with 10 per cent of sawdust, hydrated lime mixed with 10 per cent of sawdust. Rather a large proportion of catalyst was used, viz., 5g. nickel to 95 g. oil. The best results were obtained at 220°–250° C. Treatment lasted five hours. The titer of the solid product was 36°, the iodine number 66.92. The same mixture hydrogenated with hydrogen for only two hours and fifteen minutes had an iodine number of 35.7.

3287. Hydrogenation (?) of Oleic Acid with Activated Hydrogen. Waterman and Bertram³⁵ subjected the alleged hydrogenation of oleic acid by activated hydrogen³⁶ to a critical examination. The iodine value did not fall below 78, the elementary composition did not change, and the refractive index rose. Melting-point and molecular weight determinations point to a condensation of 2 molecules of oleic acid to form a dibasic acid.

³³ *Z. Unters. Nahr. Genussm.*, 1918, **35**, 313; *J.S.C.I.*, 1918, 558A.

³⁴ *Oil and Fat Ind. (Russia)*, 1926, Nos. 2–3, 45; *Chem. Abst.*, 1928, **23**, 3059.

³⁵ *Chem. Umschau*, 1927, **34**, 32.

³⁶ *Bonhoeffer, Z. Physik. Chem.*, 1924, **113**, 199.

CHAPTER XXXIII

CATALYTIC HYDROGENATION OF GLYCERIDES AND FATTY ACIDS

EXPERIMENTAL

ISO-OLEIC ACID

3300. Iso-oleic Acid. In the hydrogenation of fats containing unsaturated acids of the C_{18} series there is formed a considerable quantity of an isomer (or mixture of isomers) of oleic acid solid at ordinary temperatures. This is known as iso-oleic acid,¹ a name which, in the older literature, was used for another acid.² The distinguishing characteristic of the iso-oleic acid of hydrogenation is the insolubility of its lead salt in ether and other common organic solvents. As a general rule, the lead salts of unsaturated acids occurring in oils and fats are soluble in ether, etc.,³ and this is used to effect the separation of saturated from unsaturated fatty acids.

3301. A large body of research has been devoted to the formation of iso-oleic acid in hydrogenation. The questions asked were: How can the quantity of iso-oleic acid be estimated? What is the position of the double bond? What are the conditions of hydrogenation which favor or depress the production of iso-oleic acid?

3302. As a result of their own work on peanut oil and sunflower oil, Kaufmann and Hansen-Schmidt⁴ seem to have come to the rather drastic conclusion that hardening of oils, in practice, is due to the formation of iso-oleic acids almost exclusively. This may have been so with their technique, and undoubtedly iso-oleic acid is often an important contributory to the high melting-point of hardened fats. Nevertheless with different technique, both on the laboratory scale and in the industry, solid fats are produced from oils, which contain insufficient iso-oleic acid to account for their high melting-point and from which saturated fats can be isolated in quantity far larger than that present in the original oil.

3303. Estimation of Iso-oleic Acid. The most satisfactory method of estimating iso-oleic acid is based on a method first used (for a slightly different purpose) by Jean and afterwards modified by Twitchell. This is based on the precipitation of the solid fatty acids with lead acetate in alcoholic solution. The following is Twitchell's own description.⁵

¹ Lewkowitsch: *Oils, Fats, and Waxes*, 5th edn., I, 192.

² *Viz.*, the product obtained by the Saytzeffs by distillation of a dihydroxystearic acid.

³ Lead erucate and, perhaps, lead elaeostearate are insoluble.

⁴ *Ber.*, 1927, 60B, 50; *Chem. Abst.*, 1927, 21, 1556.

⁵ *Ind. Eng. Chem.*, 1921, 13, 807. The same method, with identical technique, is de-

3304. Weigh in a beaker as much of the fatty acid as is estimated to contain 1 to 1.5 g. of solid acids. In the case of a very liquid oil this amount will be about 10 g., while in the case of tallow it will be only 2 or 3 g. Dissolve in 95 per cent alcohol. The total alcohol for the two solutions should be about 100 cc. Heat both solutions to boiling and pour the lead acetate solution into the solution of fatty acid. Allow to cool slowly to room temperature, and then for several hours, preferably over night, to about 15° C. Filter and test the filtrate for lead with a few drops of an alcoholic solution of sulphuric acid. If there is no precipitate showing that lead is not in excess, the analysis must be repeated, using less fatty acid or more lead acetate. Wash the precipitate with 95 per cent alcohol until a sample of the washings diluted with water remains clear. Transfer and wash the precipitate from the filter back into the beaker, using about 100 cc. of 95 per cent alcohol. Add 0.5 g. of acetic acid and heat to boiling. The precipitate will slowly dissolve. Allow to cool to room temperature and then to 15° C. as before. Filter and wash with 95 per cent alcohol as before. Transfer the precipitate by washing the filter paper with ether into the beaker. Add sufficient dilute nitric acid to decompose the lead salts. Pour and wash the whole mixture into a separatory funnel and shake. Wash with water until the washings are no longer acid to methyl orange. If a trace of nitric acid should remain with the ethereal solution it will act on the fatty acids in the subsequent drying. Transfer the ethereal solution to an evaporating dish, evaporate, dry, and weigh. If desired, larger quantities of material than those given above can easily be handled.

3305. If in the above process insufficient lead acetate is used to precipitate all of the solid acids, the precipitation is fractional, and the solid saturated fatty acids of higher molecular weight come down first. In this case liquid acids are not carried down with the solid and a second precipitation is not required. For example:

3306. Thirty grams of peanut-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 12°, yielded 1.6935 g. of solid acids having a mean combining weight of 317.

3307. Thirty grams of olive-oil fatty acids, treated with 1 g. of lead acetate in 200 cc. of 95 per cent alcohol and cooled to 11°, yielded 1.3770 g. of solid acids having a mean combining weight of 266 and an iodine value of 0.79.

3308. Position of Double Bond in Iso-oleic Acids. Moore,⁶ who made an elaborate examination of the whole problem of iso-oleic acid and its formation in hydrogenation, concluded that this acid was a mixture of isomers of different stability. The first of these would be a $\Delta_9:10$ acid, the second, apparently, a $\Delta_9:10$ isomer. Ordinary liquid oleic acid was also a $\Delta_9:10$ acid: the $\Delta_9:10$ component of hydrogenation iso-oleic acid would, therefore, have to be the well-known elaidic acid, since no third isomer with the same linkage was possible.⁷

3309. A recent investigation⁸ by a searching method leads to the conclusion that an iso-oleic acid produced during the hydrogenation of arachis (peanut) oil has a double bond in the 12-13 position. This, seemingly, results from the hydrogenation of the 9-10 double bond in linoleic acid, leaving the 12-13 bond unsaturated. The method used was: The mixed free acids were ozonized. The free acids and the acid esters of the resulting dicarboxylic acids were extracted with dilute sodium carbonate solution and liberated with sulphuric acid: this was followed by steam distillation. The products were decamethylene-dicarboxylic acid (12 + 1 carbons), caproic acid (5 + 1 carbons), and a trace of azelaic (nonane-di-) acid, this last attributable to the presence of a small quantity

scribed by Davidsohn and Streichhahn as "Grün's method" in *Seifensieder Ztg.*, 1926, **53**, 551; *Chem. Abst.*, 1926, **20**, 3828.

⁶ *J.S.C.I.*, 1919, **38**, 320T.

⁷ The Saytzeff's acid which was at first thought to be an α - β acid ($\Delta_2:3$), melted at 42° C. and was soluble in alcohol. Lesueur (*J. Chem. Soc.*, 1904, 1711) synthesized an α - β acid, m.p. 58°-59° C., insoluble in alcohol.

⁸ Bauer and Mitsotakis. *Chem. Umschau Fette, Oele, Wachse u. Harze*, 1928, **35**, 137.

of ordinary oleic acid. The double bond in an iso-oleic acid may be anywhere except at the 9-10 position which gives the ordinary oleic acid [or elaidic acid].

3309A. Hilditch and Vidyarthi^{8a} studied the partial hydrogenation of higher mono- and polyethylenic esters. Methyl oleate, palmitoleate, and erucate were treated with hydrogen at 114–220° in the presence of nickel mounted on kieselguhr (15 per cent Ni), the concentration of metallic nickel present with respect to the ester being about 0.5 per cent, until their iodine values were reduced by about 30 per cent. The products of hydrogenation were examined by oxidation with potassium permanganate in hot acetone solution, with formation of free monocarboxylic acids and monomethyl ethers of dicarboxylic acids, together with neutral (non-oxidized) material of negligible iodine value. The evidence afforded by the identification of the dicarboxylic acids (and to a smaller extent of the monocarboxylic acids) indicates that the isomeric acids produced during hydrogenation consist in each case of a mixture of acids in which the ethylenic linking is adjacent to the position occupied in the original compound, and that these acids, together with the original position isomeride, are almost certainly present in both *cis*- and *trans*-forms in the hydrogenated products. The proportion of *iso*-acids formed appears to vary with the length of the carbon chain.

3309B. In the case of higher polyethylenic esters the conclusions to be reached from the acids isolated as scission products from the oxidized esters are complicated by the facts that (a) the hydrogenation process is selective, not only as regards the degree of unsaturation present, but also to a considerable extent in that each ethylenic linking is not equally attacked, and (b) isomerization occurs, although to a smaller degree. Hilditch and Vidyarthi say that it can be deduced with certainty that the unsaturation in linoleic acid is in the Δ^1 - and Δ^2 -positions, while in linolenic acid the positions of the Δ^1 and Δ^2 linkings can be fixed, but it can only be indicated that the third double linking lies beyond the fourteenth carbon atom of the chain.

3310. In the reduction of alpha-elaeo-stearic acid⁹ (as its ethyl ester) a 10-11 iso-oleic acid, m.p. 52°–53° C., was obtained from the product of the first step which was a 10-11 and 12-13 linoleic acid. The positions were determined by ozonization.

3311. Conditions of Formation of Iso-oleic Acids. A discussion of the conditions favoring or depressing the formation of iso-oleic acid during hydrogenation would cover almost the same ground as an account of selective hydrogenation of fatty oils. The latter subject is considered in paragraphs 3314 *et seq.*, to which the reader is referred. There is some contradiction among the results reported: it seems fairly clear, however, that with a given catalyst high temperature and long operating time favor the formation of iso-oleic acid. In connection with the effect of operation time it is important to remember that iso-oleic acid may certainly be formed during hydrogenation of ordinary oleic acid¹⁰ and

^{8a} *Proc. Roy. Soc.*, 1929, A **122**, 552–570; *Brit. Chem. Abst.*, **1929**, 423A.

⁹ Böeseken and v. Krimpen, *Verslag Akad. Wetenschappen Amsterdam*, 1928, **37**, 66; *Chem. Abst.*, 1928, **22**, 1953.

¹⁰ Moore, *loc. cit.* Cf. para. 3772.

that dehydrogenation of stearic acid may occur, under some working conditions, yielding an oleic acid isomer.

3312. In hydrogenating oleic acid in the vapor phase Shaw ¹¹ obtained some curious results. Shaw used a glass tower packed with nickel reduced on pumice. This was maintained at 300° C. Oleic acid vapor (iodine number 79) and hydrogen were passed over the catalyst. At 100-mm. pressure a reduction of 5 per cent in the iodine number was obtained. A second passage produced no further reduction. Fresh oleic acid was used and again a 5 per cent reduction resulted: therefore the catalyst was still active. At 150 mm. the iodine number was 68 to 70. At 200 mm. 20 per cent reduction was obtained.

3313. These results suggested the possibility of an equilibrium between stearic acid, oleic acid and hydrogen, and that the reduction degree which Shaw found varied from pressure to pressure was constant for any one pressure. If this conclusion were correct, then the equilibrium should be reached from the opposite end, namely through distilling stearic acid in the presence of hydrogen. In order to see whether this were possible stearic acid was treated in exactly the same way as the oleic acid by distilling through freshly prepared catalyzer. As a result of the test it appeared that stearic acid experienced no change in iodine number, which apparently excluded the idea that conditions of equilibrium were involved.

Shaw's observations that by repeated distillation of oleic acid no further reduction occurs was not to be explained on the ground of fractional distillation of the partially reduced product, for the entire contents of the flask were distilled through the catalyzer, and furthermore the boiling-point of stearic acid differs very little from oleic acid, so Shaw is at a loss to explain the cause of this peculiar behavior after finding it not due either to the existence of equilibrium or fractional distillation.

SELECTIVE HYDROGENATION OF OILS

3314. Acids with More than One Double Bond—Order of Saturation. When a fatty acid has more than one double bond, what happens when it is catalytically hydrogenated? Are all the bonds simultaneously saturated, in any given molecule, so that a fully saturated acid is formed from the first? If not, in what order are the double bonds saturated? This problem has stimulated a great deal of experimental research. The most elaborate and painstaking work on this subject seems to be that of Richardson, Knuth and Milligan.¹²

3315. The difficulty that has beset this kind of work is largely due to the formation, during hydrogenation, of a solid isomer of oleic acid, iso-oleic acid.¹³ The usual method of determining the relative amounts of saturated and unsaturated acids has been to separate the lead salts with ether. The lead salts of

¹¹ *Seifen. Ztg.*, 1912, 713.

¹² Heterogeneous Catalysis. I. Selective action of nickel in hydrogenation of certain vegetable oils, *Ind. Eng. Chem.*, 1924, 16, 519. II. Hydrogenation of Marine Oils, *Ind. Eng. Chem.*, 1925, 17, No. 1, 80. The first article contains a critical review of previous work.

¹³ Lewkowitsch, *Chem. Tech. Oils*, Vol. I, 192. Also see paras. 3300-3313, this volume.

liquid-saturated acids are insoluble in ether. Unfortunately, the lead soap of iso-oleic acid, also, is practically insoluble in ether as noted in paragraph 3300. This leads to a result which, calculated back to the whole body of fatty acids, gives too high a proportion of linoleic acid relatively to oleic acid. It might appear that this could have been corrected by determining the iodine number of the solid fatty acids and calculating this iodine absorption to iso-oleic acid. Unfortunately there is a fallacy here owing to the persistence of an iodine-absorbing salt in the solid lead salt mixture, even when iso-oleic acid is known to be absent. However, the general results in the case of vegetable oil were fairly concordant. The conclusion was that, in a mixture containing glycerides of fatty acids of different degrees of unsaturation (oleic, linoleic, linolenic), there occurs selective hydrogenation, i.e., the acids of higher degrees of unsaturation are hydrogenated down to the oleic acid stage before any substantial amount of saturated acid is formed.

3316. This conclusion was confirmed by the work of Richardson and his collaborators, indeed the selectivity of hydrogenation of vegetable oils was found to be even greater than had been thought. It was also brought out that increase in the amount of (nickel) catalyst favored selectivity, which effect was also obtained by increase of the temperature of operation, up to 200° C. The theoretical implications are of interest. They tend to confirm the view of Armstrong and Hilditch ¹⁴ that hydrogen absorption by a given unsaturated compound in the presence of nickel proceeds normally at a constant rate of reaction. Other observers believed that their results justified them in regarding the reaction as unimolecular: for this to be true each of the components should have been hydrogenated *from the very beginning* at rates proportional to the product of the concentration and the reaction constant of each component (catalyst, temperature and hydrogen pressure being maintained constant). The velocity of conversion of oleic acid to stearic acid seems to be decidedly lower than that for linoleic to oleic acid. We may, perhaps, picture the active catalytic surface (on Taylor's hypothesis) as better shaped to hold the linoleic (linolenic, etc.) than to hold the oleic molecules in position for hydrogenation.

3317. The second article by Richardson and his co-workers deals with the hydrogenation of marine oils. This work is complicated by the fact that the unsaturated fatty acids of marine oils consist largely of members with more than 18 carbon atoms to the molecule. This appears to be true equally of mammal (whale) oil ¹⁵ and of fish oil. The technique employed was therefore modified as will presently be explained.

3318. It appears that the hydrogenation of whale oil in the presence of catalytic nickel results initially in the preferential conversion of the highly unsaturated C₂₀ and C₂₂ acids to acids of either one or two double bonds without the formation of substantial quantities of saturated acids. At an iodine value of approxi-

¹⁴ *Proc. Roy. Soc.*, 1919, **96A**, 137; *J. Soc. Chem. Ind.*, 1920, **79**, 120.

¹⁵ Milligan, Knuth and Richardson, *J. Am. Chem. Soc.*, 1924, **46**, 157. The unsaturated fraction of fatty acids from whale oil was about 80 per cent of total; of this a little less than half was composed of C₂₀ and C₂₂ acids with some C₂₄ acid.

mately 84, the character of the hydrogenation changes abruptly. Immediately below this critical point, hydrogenation results in the formation of substantial amounts of palmitic and stearic acids, while the C_{10} and C_{12} acids containing two double bonds are simultaneously converted to corresponding acids of one double bond, possibly with the formation also of very small amounts of saturated acids of 20 and 22 carbon content. Even at an iodine value of 57, substantial quantities of unsaturated acids containing two double bonds are present in the hydrogenated oil.

Menhaden oil behaves in a similar manner on hydrogenation, and on account of similarity in composition it is probable that the same will be found true of other marine oils. It must, however, be regarded as mere coincidence that the critical points in the hydrogenation of the particular samples of whale oils and of menhaden oil used in this investigation were reached at practically identical iodine values.¹⁶

3319. In the work on vegetable oils Richardson and his collaborators employed the method of Jean as used by Twitchell¹⁷ in which the lead soaps of the solid acids are fractionally precipitated from an alcoholic solution of the mixed acids, by the addition of a solution of lead acetate. Working on the solid acid fraction they determined (1) the weight, (2) the iodine number and (3), on the original oil, the iodine number of the mixed fatty acids. This method had the limitations that the calculations to (1) solid saturated acids, (2) solid unsaturated acids, (3) oleic acid and (4) linoleic acid would be possible only if the sample contained no unsaturated acids except oleic and linoleic (or isomers) and no saturated acid below C_{16} (the lead salts of myristic and lower saturated acids being too soluble in alcohol). Therefore, for the work on marine oils the fatty acids were separated by fractional distillation of the methyl esters by the method previously employed by the same workers.¹⁸

3320. Marcusson and Meyerheim¹⁹ had reached the conclusion that train oil did not hydrogenate selectively or by stages, that is to say, the more highly unsaturated components did not largely take up hydrogen before olein becomes converted into stearin. A certain percentage of the highly unsaturated fatty acids remained even after a large proportion of the oleic acid had been transformed into stearic acid. The inner iodine number (iodine number of the liquid fatty acids) of a sample of hardened train oil was found to be 107, which result led to the foregoing conclusion.

Abstracts of Articles on Selective Hydrogenation of Oils

3321. Moore, Richter and van Arsdell. The incomplete hydrogenation of cottonseed oil. *J. Ind. Eng. Chem.*, 1917, **9**, 451. A long and detailed article notable for its development of the triangular diagram in the study of hydrogenation. Lead-salt-ether method with its defects, was used. Effect of pressure, temperature, percentage of catalyst, agitation and

¹⁶ *Ind. Eng. Chem.*, 1925, **17**, 80.

¹⁷ *Ind. Eng. Chem.*, 1921, **13**, 806. See para. 3304 on page 340, this volume, for technique.

¹⁸ *J. Am. Chem. Soc.*, 1924, **46**, 157.

¹⁹ *Zeit. f. angew. Chem.*, 1914, No. 28, 201.

foreign bodies is studied. Sulphur and sodium sulphide were found to poison the catalyst. A *locus classicus* for selectivity, though many of the conclusions have since been revised.²⁰

3322. Armstrong and Hilditch: *Proc. Roy. Soc.*, 1919, **96A**, 137. Catalytic actions at solid surfaces. I. Hydrogenation of unsaturated fats in the liquid state in the presence of nickel. Comparison of enzyme action and that of catalysis at solid surfaces. Hydrogenation of whale oil proceeds at constant rate to a defined breaking-point, which is said to occur when the proportion of glycerides with acids more unsaturated than oleic acid fell to 10 per cent (but see Richardson *et al.*, *loc. cit.* for a criticism of this conclusion). This statement is reaffirmed in the article by Hilditch and Moore.

3323. Hilditch and Moore. Selective hydrogenation. *J.S.C.I.*, 1923, **42**, 15T. Further evidence in support of the statement²¹ that the rate of hydrogenation of any pure mixture of olein and glycerides less saturated than olein, when plotted as the amount of hydrogen absorbed against time, consists of two phases: (1) a linear graph to a certain point, (2) a further sector at first linear then curved. This point is said to have invariably occurred when only 10 per cent of the linolein remained unhydrogenated. In the case of natural oils the amount of saturated derivatives did not increase until the amount of linolein had fallen to 10 per cent of the mixture. The free fatty acids from cottonseed oil presented an exception to this rule. Discussion of the mechanism of selectivity, favoring Armstrong-Hilditch hypothesis of unstable intermediate compounds between catalyst and reactants.

3324. Moore.²² The formation of solid iso-oleic acids by the hydrogenation of ordinary liquid oleic acid. *J.S.C.I.*, 1919, **38**, 320T. An important contribution to the iso-oleic acid problem. Experimental and critical. According to Moore, iso-oleic acid is formed only during the actual hydrogenation of oleic acid (this is not universally accepted (see Ubbelohde and Svanoe, *infra*). Iso-oleic acid is a mixture of isomers one of which is elaidic acid while the other (or others) is formed by migration of the ethylenic linkage. Palladium causes a much larger formation of iso-oleic acid than does nickel, at the temperature used by Moore, viz., 180° C.

3325. Lush. Hydrogenation. *J.S.C.I.*, 1923, **42**, 219T. A general article dealing with compact or massive nickel catalysts, and especially with the Lush-Bolton anodic-oxidized catalyst. Two methods are contrasted as to the production of iso-oleic acid: oil flowing as a film gives less of this solid isomer than an overflow method. See para. 3752.

3326. Lush. Kinetics of Hydrogenation. I. *J.S.C.I.*, 1924, **43**, 53T. The formation of iso-oleic acid is favored by high operating temperatures (190° C.): This isomer is probably a dehydrogenation product. There is some evidence that the reaction velocity is proportional to the square root of the hydrogen pressure and is linear. This is in favor of an activated atomic hydrogen theory.

3327. II. *J.S.C.I.*, 1925, **44**, 129T. Further discussion of the reactions and conditions involved in hydrogenation. With oil in excess and hydrogen limited, the velocity is linear and proportional to the hydrogen pressure. With increased access of hydrogen the velocity remains linear and is proportional to the square root of the pressure. With accumulation of saturated oil the reaction becomes unimolecular.

3328. According to Ueno and Okamura the amount of iso-oleic acids increases with the temperature and with the length of time of hydrogenation. The oil used was plaice oil.²³

3329. These workers had already reported the same results with cottonseed oil,²⁴ and Ueno and Kuze had observed the temperature effect (with a nickel catalyst) in the hydrogenation of chrysalis oil.²⁵

3330. Kaufmann and Hansen-Schmidt²⁶ making periodical determination of the iodine and thiocyanogen values during the course of mild technical hydrogenation of peanut oil show that oleic acid is not reduced, and that the main part in the change is played by linoleic acid, which is converted into singly unsaturated acids solid at the atmospheric temperature; the proportion of saturated components remains unchanged. More prolonged hydrogenation of sunflower oil causes an increase in saturated compounds at the expense of linoleic acid, the bulk of which is, however, transformed into singly unsaturated acids. Subsequently, reduction of oleic acid and of its intermediately formed isomerides commences. Simultane-

²⁰ See paras 3245 *et seq.*

²¹ Armstrong and Hilditch. *Loc. cit.*

²² C. W. Moore. The collaborator of Richter and van Arsdell is H. K. Moore.

²³ *J. Soc. Chem. Ind. (Japan)*, 1927, **30**, 817.

²⁴ *Ibid.*, 71.

²⁵ *Ibid.*, 1926, **29**, 75.

²⁶ *Ber.*, 1927, **60B**, 50; *Suppl. J.S.C.I.*, B, 1927, 226.

ously, displacements of the double linking occur (recognized by the discrepancy between the iodine and thiocyanogen values) which are due to dehydrogenation in an unexplained manner.

3331. Schestakoff and Kuptschinsky. *Z. deutsch. Oel u. Fettind.*, 1922, **42**, 741, 757 and 774; *Chem. Zentr.*, 1923, **94**, ii, 420; *J.S.C.I.*, 1923, **42**, 364A. Experimental investigation of the velocity of hydrogenation of linseed, hempseed and sunflower seed oils. Hydrogenation of oleic acid proceeds more slowly than that of linoleic acid. The velocity diminishes in the order linolenic, linolic, oleic. The relation of titer (melting-point of mixed fatty acids) and iodine value in natural solid fats and in hardened oils is discussed. Owing to the presence of palmitic and myristic acids in natural fats the titer of the latter is lower for the same iodine value than that of the product of hydrogenation.

3332. Koss. Catalytic reduction of unsaturated fats. *Przemysl Chem.*, 1920, **4**, 39; *Chem. Zentr.*, 1920, **91**, IV., 442; *J.S.C.I.*, 1920, 755A. Discussion of the activity of nickel oxides. Discussion of the influence of the position of ethylenic linkages on the hydrogenation of glycerides. Double bonds between the 9th and 10th and between the 12th and 13th carbon atoms are easily reduced; that between the 15th and 16th is slowly attacked. The farther a double bond is from the carboxyl group the more difficult it is to reduce.

3333. Richardson and Snoddy. *Ind. Eng. Chem.*, 1926, **18**, 570. With platinum catalysts selectivity is favored by increasing temperatures, in the hydrogenation of cottonseed oil. The selectivity is less than with nickel.

3334. Ubbelohde and Svanoe. *Z. angew. Chem.*, 1919, **32**, 257, 269, 276; *J.S.C.I.*, 1919, 870A. A study of the hydrogenation of whale oil. The increase in the rate of absorption due to rise of temperature is said to stop at 200° C.; an acceleration was also noted with increase in the amount of catalyst up to 2.4 per cent of the particular catalyst used. The analytical difficulties caused by the formation of iso-oleic acid are noted. Iso-oleic acid is believed to be formed both from linoleic acid and from oleic acid.

3335. Williams. Selective Hydrogenation. *J.S.C.I.*, 1927, **46**, 456T. A critical study of data, published and unpublished, to establish a measure of the degree of divergence from complete selectivity in any given case. For a given oil the degree of selection is a linear function of temperature and also of the proportion of double linkages in the original fatty mixture. In hydrogenation of acids selection is more complete with a high than with a low original iodine number; the reverse is true with the glycerides.

Williams observes that if the hydrogenation of an oil were completely selective with respect to linoleic acid, stearic acid would not be formed until a certain iodine value were reached, hence the curve relating to percentage of saturated acids in the oil with the iodine

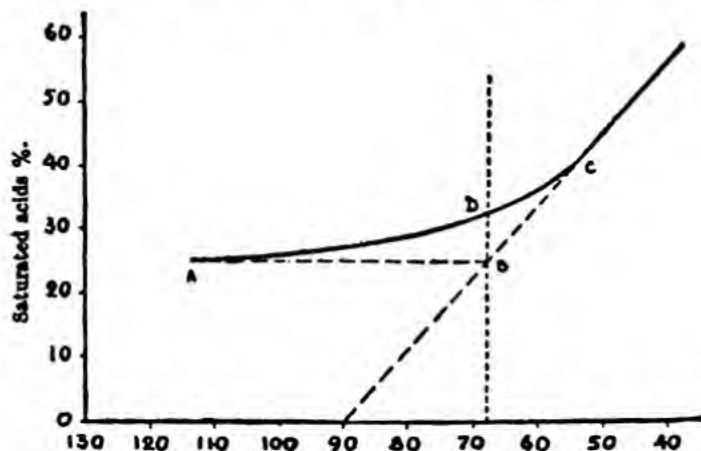


FIG. 41.—VARIATION OF THE PROPORTION OF SATURATED ACIDS IN AN OIL DURING HYDROGENATION.

values would appear as shown by the dotted line A-B-C in Fig. 41. A projection of the line B-C will intersect the iodine value at about 90 (the iodine value of oleic acid). Hydrogenation, however, is usually not completely selective and hence the curve will assume the form shown by the line A-D-C, stearic acid being formed to some extent in the early stages of the reaction.

Abstracts Relating to Experimental Hydrogenation of Oils

3336. v. Alphen. The action of phenylhydrazine and hydrazine on fats and fatty acids. *Rec. trav. chim.*, 1925, **44**, 1064; *Chem. Abst.*, 1925, **19**, 1235. Glycerides of unsaturated fatty acids yield hydrazides of the saturated acids.

3337. Amberger and Wheeler-Hill. Composition of oat oil. *Z. Unters. Lebensm.*, 1927, **54**, 417. Application of hardening to recognition of individual glycerides.

3338. Fréjacque. *Chim. et Ind.*, 1920, **4**, 443; *J.S.C.I.*, 1920, 789A. Experiments on hydrogenation of linseed oil with 1 per cent of catalyst reduced from basic nickel carbonate. With catalyst reduced dry at 160° C. the iodine value after four hours was 152; with that reduced at 240° C. it was 133. With catalysts reduced in the oil at 160° C. and 240° C., the iodine values were 70 to 80, respectively. (Contrast Roubaix on hydrogenation of oleic acid.)

3339. Dittmer. Hydrogenation of oxidized and polymerized oils, *Seifen-Ztg.*, 1927, **54**, 240; *Chem. Abst.*, 1927, **21**, 2391. Polymerized oils first depolymerize, then hydrogenate, yielding stearic acid. Oxidized oils use up more hydrogen because the oxidized product must first be reduced, before hydrogenation to stearic acid takes place. Oxidized castor oil yields hydroxystearic acid.²⁷

3340. Gonzáles. Stereoisomerism of ethylenic acids. Hydrogenation of stearolic and behenolic²⁸ acids. *Anales soc. españ. f. s. quím.*, 1926, **24**, 156. Difference in isomers produced by different methods of hydrogenation. Discussion of their stereoisomerism.

3341. *Hydroxy Acids.* The behavior of the hydroxyl group of the hydroxylated fatty acids on catalytic hydrogenation by means of nickel has been studied by Jurgens and Meigen. Nickel catalyzer reduces castor oil below 200° practically only at the double bond of the ricinolic acid radical, while above 200° its hydroxyl group is also reduced. Ricinolic acid itself is little affected at the lower temperature but its hydroxyl group is reduced at the higher temperature. Nickel oxide catalyzer reduces the hydroxyl group more rapidly than the double bond. With 2 per cent nickel catalyzer under high pressure the hydroxyl group reduction is slower than at atmospheric pressure because the increased tension of the steam from the hydroxyl group tends to prevent further decomposition of this group.²⁹

3342. Mashkilleison. Action of carbon monoxide on the nickel catalyst in oil hardening. *Oil and Fat Ind.* (Russia), Nos. 2-3, 47. Emphasizes difference between gas containing carbon monoxide and that free from it.

3343. Chemical Reactions in Fat Hardening.³⁰ Under this title Normann discusses the general reactions involved and the behavior of the nickel-kieselguhr catalyst. Graphs are given for a number of oils showing the progress and completion of hardening, the fall in iodine value and corresponding rise in melting-point, and also the fall in iodine value together with progressive fall in refractive index (Zeiss butyrorefractometer). For judging the progress of hardening in a particular case the determination at intervals of the refractive index of the oil is the quickest and is better than a method involving the measurement of the amount of hydrogen consumed. An accompanying table shows the amount of hydrogen in cubic meters at 0° and at 20° required to saturate completely 1000 kg. of the commoner fatty acids and fatty oils. Owing to loss of hydrogen and to side reactions the amount of hydrogen consumed in a particular hardening is in practice 10-20 per cent in excess of the amount as calculated from the fall in the iodine value.³¹

3344. Pelly. Notes on the hydrogenation of fatty acids and of mixtures of fatty acids with neutral oils. *J.S.C.I.*, 1927, **46**, 449T. Both with activated nickel turnings and with powder catalysts, under similar conditions of experiment: (1) Fatty acids alone are less rapidly hydrogenated than neutral oils alone. (2) When mixtures of fatty acids with neutral oil are hydrogenated, the degree of hydrogenation of the fatty acid is very considerably increased beyond that for neutral oil alone, while the degree of hydrogenation of the neutral oil in the mixture is greatly decreased. (3) The rate of hydrogenation of unsaturated glycerides is greatly retarded in the presence even of saturated fatty acids.

²⁷ Cf. on same subject Talanzer, *Oil and Fat Ind.* (Russia), 1927, No. 8, 20; *Chem. Abst.*, 1928, **23**, 3793; Laryakov, *ibid.*, No. 1, 27; *Chem. Abst.*, 1928, **23**, 4264.

²⁸ The abstract *Chem. Abst.*, 1926, **20**, 2310, has "stearic" and "behenic."

²⁹ *Chem. Umschau*, 1916, **23**, 99, 116; *Z. angew. Chem.*, 1917, **30**, II., 34; *J.S.C.I.*, **36**, 657; *Chem. Abst.*, 1917, 2736. See also paras. 3426 and 3427, page 357, this book.

³⁰ *Z. Deuts. Oel- u. Fett-Ind.*, 1926, **46**, 193-195.

³¹ *Brit. Chem. Abst.*, 1926, 552B.

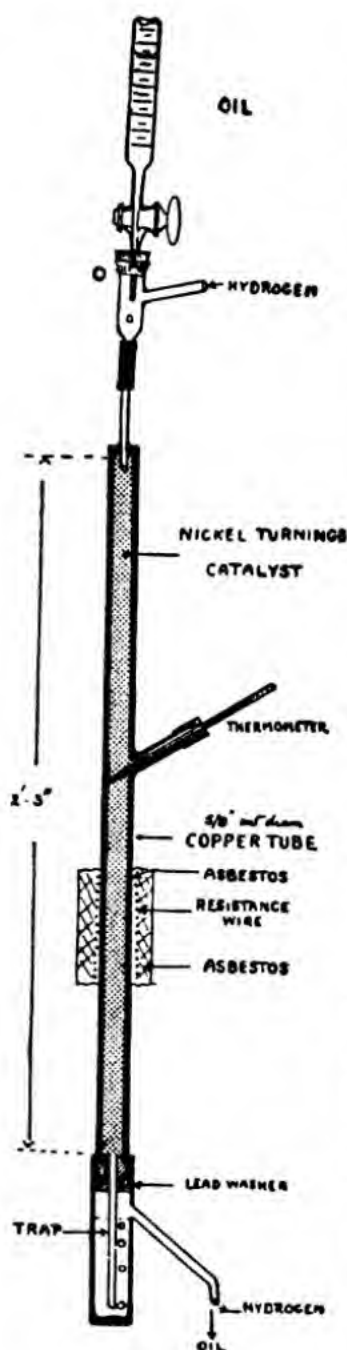


FIG. 42.

When Pelly employed nickel turnings as a catalyst these were packed in an electrically heated copper tube. The oil, supplied by a burette, was allowed to flow down over the catalyst. The apparatus employed by Pelly is shown in Fig. 42. In order to avoid any possibility of introduction of air, the exit end of the copper tube was equipped with a trap.

3345. Roubaix. Catalytic hydrogenation of oleic acid and commercial olein with nickel as catalyst. *Bull. Soc. Chim. Belg.*, 1924, **33**, 193. Pure oleic acid and the commercial product were readily hydrogenated by nickel reduced dry from the oxide or formate, with formation of only a small quantity of nickel soap. Very poor hydrogenation was obtained with catalyst reduced in the fatty acid itself and there was an excessive production of nickel oleate. No nickel stearate was formed.

3346. Smith and West. Reduction [i.e., dehalogenation] of linolenic and linolic (linoleic) bromides and re bromination of the free acids. *Philippine J. Sci.*, 1927, **33**, 297. Examination of the stereoisomers: molecular rearrangements. An apparatus and procedure for dehalogenation of these compounds are described. A full abstract of the results will be found in *Chem. Abst.*, 1927, **31**, 2250.

3347. Sweeney and Ellert. Evidences of auto-catalysis in the hydrogenation of cotton-seed oil (with cobalt catalyst). *Science*, Jan. 14, 1921, 20.

3368. Ueno. Velocity of the hydrogenation of oils. *J. Chem. Ind., Tokyo*, 1918, **21**, 749. The velocity of the reaction obeys the law of unimolecular reactions. The conditions were: catalyst, nickel-kieselguhr 1-3; temperature 100°-160°; substrate, soya-bean, camellia and sardine oils.

3349. West and Gonzaga. Effect of composition on the complete hydrogenation of some Philippine oils with nickel catalyst. *Philippine J. Sci.*, 1923, **23**, 277. Lum bang, pili nut and cocoanut oil were hardened to a negligible or zero iodine number. Palomaria oil gave neither a hard fat nor a low iodine number.

3350. Williams. The melting-point of hydrogenated cottonseed oil. *J.S.C.I.*, 1927, **46**, 448. Owing to the effect of the temperature of hydrogenation on selectivity, by determination of iodine number and the melting-point, the temperature of hydrogenation may be estimated "to within about 10°" ($\pm 10^\circ$ or $\pm 5^\circ$? The former figure would give rather a wide range—say 160°-180° C.)

3351. Limit of unsaturation in menhaden oil. McGregor with Beal, *J. Am. Chem. Soc.*, 1926, 3152. Determination of mixed melting-points.

CHAPTER XXXIV

CATALYTIC HYDROGENATION OF FATTY OILS

ANALYTICAL METHODS AND DATA

I. THE ANALYTICAL CONSTANTS OF HYDROGENATED OILS ¹

3400. The hydrogenation of oils has to such an extent changed certain of the constants by which oils and fats are at least in part identified, namely, the iodine number and the specific gravity, that the identification of a fat or fatty mixture, often heretofore a troublesome matter at best, now promises to become even more difficult.

3401. The reduction of the iodine number through the introduction of hydrogen into the oil, in a sense, is arbitrary; there is no difficulty in reducing the iodine number almost to zero through the hydrogenation process, or at any moment to interrupt the operation and from one and the same initial material to produce products having the most varied iodine numbers.

3402. The specific gravity and melting-point advance hand in hand as saturation progresses, the specific gravity approaching that of tristearin, while the resultant melting-point in considerable measure depends upon the molecular weight and the hydroxyl content of the fatty acid components of the oil. The specific gravity of a hardened cottonseed oil whose iodine number had been reduced to zero was found by Normann and Hugel ² to be 0.9999 at 15° C., while they note that tristearin has a specific gravity of 1.0101 at the same temperature. ³

3403. The index of refraction also is strongly modified. A sample of fish oil at 56° C., according to Normann and Hugel, showed a figure of 53.8; while after hardening to an iodine number of 22.5 the index was 36° at the same temperature (scale of the Zeiss butter refractometer).

3404. Observations made in Ellis's laboratory on the index of refraction of a number of hydrogenated oils gave the results noted below: ⁴

¹ *Jour. Ind. Eng. Chem.*, 1914, 117.

² *Chem. Ztg.*, 1913, 815.

³ The specific gravity of tristearin is given by the Chemiker Kalender as 1.0101 at 15° C., while Lewkowitch reports the specific gravity of a specimen of not quite pure stearin in the melted state as 0.9235 at 65.5 C.

⁴ A sample of hydrogenated cottonseed oil used extensively in this country exhibited a refractive index of 1.4492 and a melting-point of 59.9° C.

INDEX OF REFRACTION AT 55° C.

(Abbé Refractometer)

	Original Oil	Hydrogenated Oil
Corn	1.4615	1.4514 (M.P. 55.7° C.)
Whale (No. 1)	1.4603	1.4550 (M.P. 41.5° C.)
Soya bean	1.4617	1.4538 (M.P. 50.3° C.)
Cocoanut oil ("olein")	1.4429	1.4425 (M.P. 24.7° C.)
Linseed	1.4730	1.4610 (M.P. 42.3° C.)
Palm	1.4523	1.4517 (M.P. 38.7° C.)
Palm	1.4523	1.4494 (M.P. 44.8° C.)
Peanut (edible)	1.4567	1.4547 (M.P. 34.7° C.)

3405. It is of interest to note that while the addition of *hydrogen* to fatty oils reduces the index of refraction, the addition of *oxygen* increases the index as is shown in the case of blown or ozonized oils.

3406. The gradual reduction of the index of refraction by progressive hydrogenation is shown in the following table compiled from determinations made in Ellis's laboratory. Cottonseed oil was hydrogenated for a period of ten hours and samples were drawn at one-hour intervals.

	Melting-point	Index of Refraction, 55° C.
Original oil	1.4588
1 hour	28.2° C.	1.4577
2 hours	31.3	1.4568
3 hours	34.3	1.4557
4 hours	37.9	1.4549
5 hours	40.8	1.4540
6 hours	43.8	1.4527
7 hours	45.6	1.4518
8 hours	47.3	1.4510
10 hours	55.9	1.4496

The articles noted below may be consulted on the same subject:

3406A. Chenevean. Relation between refractive index and iodine value of oils. *Chimie et industrie*, 1926, **15**, 780; *C. A.*, 1926, **20**, 2589.

3406B. Watson and Sudborough. Relation between iodine values and refractive indices of hardened oils. *J. Ind. Inst.*, 1924, **7**, 81. Iodine values and refractive indices for oils of different degrees of hydrogenation are recorded for argemone, English mustard, Indian rape, cashew kernel, soya bean, poppy-seed, rayan, olive, seal, and cod-liver oils. Rocket, mustard, and rape oils have higher refractive indices for a given iodine value than all the other oils examined except castor and argemone oils, this being attributed to the presence of glycerides of erucic acid. The high ratio of refractive index to iodine value for argemone oil is not due to glycerides of erucic acid, but to diglycerides and glycerides of hydroxy-acids. The refractive index for completely hardened olive oil (n_D^{50} 1.4463) agrees very closely with that of the purest tristearin (1.4462). Most of the curves are approximately parallel, but that for seal oils is exceptional and crosses most of the others.

3406C. Markman and Sergejev [*Oil Fat Ind.* (Russia), 1925, No. 7, 27; *Chem. Centr.*, 1925, ii, 2418] were unable to find any definite constant relation between titer and refractive index during hardening.

3407. Crossley ⁵ reports some work carried out by Passmore on the effect of hydrogenation of a number of fatty acids and oils which is illustrated by the figures contained in the following table:

	Per Cent Nickel Used	Temperature	Time in Hours	Iodine Value		Melting-point	
				Of Original Substance	Of Product	Of Original Substance	Of Product
Ricinoleic acid.....	3	180°	2	89.8	7.99	Liquid	53°
Ricinoleic acid.....	6	100°	4	91.8	30.69	Liquid	72°
Erucic acid.....	10	180°	1	120.3	5.95	Liquid	58.5°
Erucic acid.....	3	180°	1	74.0	2.05	34°	79°
Linoleic acid.....	3	240°-250°	2	182.1	30.00	Liquid	60.5°
Linoleic acid.....	3	180°	2	176.0	7.79	Liquid	66°
Linoleic acid.....	6	100°	3	179.2	5.98	Liquid	65°
Oleic acid.....	3	240°-250°	1	82.9	4.08	Liquid	63°
Oleic acid.....	1	100°	1½	82.1	9.77	Liquid	61°
Oleic acid.....	6	100°	2	84.8	3.83	Liquid	63°
Whale oil.....	3	180°	1½	120.0	10.30	Liquid	54°
Whale oil.....	3	240°-250°	1½	123.0	27.7	Liquid	48.5°
Cod oil.....	3	240°-250°	1½	157.0	13.1	Liquid	56°
Cod oil.....	3	180°	3	159.5	11.1	Liquid	57°
Linseed oil.....	3	240°-250°	1½	181.2	9.52	Liquid	66°
Linseed oil.....	10	180°	1	176.8	4.75	Liquid	62.5°
Rape oil.....	3	180°	1½	118.2	11.2	Liquid	59°
Rape oil.....	3	100°	10½	119.1	24.3	Liquid	56°
Cottonseed oil.....	3	175°	1½	101.8	18.5	Liquid	58°
Fish oil.....	2	190°-200°	6	124.5	51.5	Liquid	Solid
Almond oil.....	2	172°-185°	6	92.1	22.6	Liquid	

3408. Three fats obtained by Knapp from a clear cottonseed oil, hardened by hydrogen with the help of different catalysts, gave the following figures:

Catalyst	Percentage of Catalyst	Character of Product	Butyro-refraction Corrected to 40° C.	Melting-point, °C.
Nickel.....	1.00	Hard	45.7	49
Platinum.....	0.10	Hard	47.8	46
Palladium.....	0.06	Brittle	45.5	52

The keeping properties of these hardened oils were found to be remarkably good. Although prepared nearly a year and a half previously and having often been exposed to damp air, yet they showed no signs of rancidity. The free acidity (0.70 per cent as oleic acid) did not appreciably change during the period of observation.⁶

⁵ *Pharm. J.*, 1914, **92**, 604, 637, 676; *J.S.C.I.*, 1914, 1135.

⁶ *Analyst*, 1913, 102.

3409. Bömer ⁷ examined a number of hardened oils and his results are condensed into the following table:

Oil	Appearance	Melt- ing- point	Solidi- fying- point	Refrac- tometer at 40°	Acid Num- ber *	Sapon- fication Num- ber	Iodine Num- ber
Peanut oil un- treated	Yellow liquid	56.8	1.1	191.1	84.4
Peanut oil hardened	White tallowy	51.2	36.5	50.1	1.0	188.7	47.4
Sesame oil hardened	White tallowy	62.1	45.3	38.4	4.7	188.9	25.4
Cottonseed oil hardened	Yellowish lard- like	38.5	25.4	53.8	0.6	195.7	69.7
Cocoanut oil un- treated	White soft	25.6	20.4	37.4	0.3	255.6	11.8
Cocoanut oil hardened	White lard-like	44.5	27.7	35.9	0.4	254.1	1.0
Whale oil hardened	Yellowish tallowy	45.4	33.7	49.1	1.1	193.0	46.8

* Milligrams potassium hydroxide for 1 g. fat.

† Determined at 50° C.

The solid and liquid fatty acids separated from the hydrogenated fat by the method of Farnsteiner showed the following properties:

Oil	Solid Fatty Acids		Liquid Fatty Acids	
	Melting- point	Acid Number	Refraction at 40° C.	Iodine Number
Peanut oil untreated	47.6	91.8
Peanut oil hardened	199.7	42.9	82.9
Sesame oil hardened	56.4	199.5	44.7	88.9
Cottonseed oil hardened	45.0	206.8	48.3	115.6
Whale oil hardened	199.5	44.4	96.0

3410. Samples of these hardened oils were examined for cholesterol and phytosterol. Hardened peanut oil was found to contain 0.4 per cent, sesame oil 1.9 per cent, cottonseed oil 1.6 per cent and whale oil 0.2 per cent of sterol, of which the three first-mentioned hardened products exhibited the typical crystalline form of phytosterol. The melting-point of these sterols ranged from 132° to 139° C., yielding acetates melting between about 126° and 129° C. The hardened whale oil gave a sterol melting at 149.7° C.

3411. Bömer made a series of fractional crystallizations of hardened oil and from a sample of hydrogenated peanut oil obtained tristearin (amounting to about $\frac{1}{3}$ per cent). Bömer has called attention to the rather striking behavior of cocoanut oil. He calculated from the iodine number that the natural oil contained 13 per cent of oleic acid and after hydrogenation approximately about 1 per cent of this acid was present. As a result of the transformation of 12 per

⁷ *Chem. Rev. u. d. Fett u. Harz Ind.*, **1912**, 220.

cent of oleic acid into stearic acid, the melting-point increased from 25.6° to 44.5° C., or thus 18.9° C., while the solidifying-point advanced from 20.4° to 27.7° C., or only 7.3° C.

3412. Bömer ⁸ has studied the melting-points of hydrogenated oils and as regards hydrogenated peanut and sesame oil he notes that the melting-points of the least soluble glycerides are very high, being 70.6° C. and 71.5° C. respectively, while the corresponding fatty acids melted at 68.6° C. and 68.5° C.; hence these glycerides apparently consist of tristearin. The hydrogenated cottonseed oil examined yielded a mixture of glycerides of melting-point 61.3° C. and derived fatty acids melting at 38° C.

3413. THE ANALYTICAL CONSTANTS OF HARDENED OILS

(According to Lehmann (*Chem. Ztg.*, 1914, 798.)

Hardened Oil	Melting-point °C.	Solidifying-point °C.	Difference °C.	Acid Number*	Saponification Number	Iodine Number †	Appearance
Peanut oil	42.8	31.6	11.2	1.0	188.2	59.0	White, tallowy
Peanut oil	35.5	24.5	11.1	1.0	188.5	62.6	White, tallowy
Peanut oil	37.8	27.0	10.8	2.1	186.9	59.5	White, tallowy
Peanut oil	37.7	26.8	10.9	White, tallowy
Sesame oil	35.2	24.2	11.0	3.0	185.0	65.6	White, lardlike
Sesame oil	36.9	24.4	11.5	3.1	190.2	64.9	White, tallowy
Sesame oil	35.8	24.5	11.3	White, tallowy
Cottonseed oil . .	30.0	18.2	11.8	0.3	193.7	70.9	Yellow, lardlike
Cottonseed oil . .	33.6	21.8	11.8	0.4	192.5	69.0	Yellow, tallowy

* Milligrams of caustic potash per gram of fat.

† Hübl Method.

3414. The iodine values of hydrogenated oils which before hardening had high iodine numbers have been determined by Kelber and Rheinheimer ⁹ using the methods of Gaebel, Hübl, and Wijs and concordant results were obtained by all three methods provided a sufficiently long time was allowed for the action of the iodine solution.

3415. Data on hardened oils by Davidsohn ¹⁰ are tabulated below:

	Melting-Point °C.	Acid Number	Saponification Number	Moisture	Ash
Talgol	39.3	3.4	191.0	0.10	0.07
Talgol extra	46.5	3.5	191.3	0.13	0.05
Candelite	49.0	3.2	191.0	0.20	0.08
Candelite extra	51.9	3.9	190.8	0.15	0.04
Coryphol	79.3	3.3	189.9	0.18	0.05

⁸ *Z. Unters. Nahr. Genussm.*, 1914, 153; *J.S.C.I.*, 1914, 323.

⁹ *Arch. Pharm.*, 1917, 417; *J.S.C.I.*, 37, 34A; *Chem. Abst.*, 1918, 1004. The chemical constants of linseed oil before and during hydrogenation have been determined by Vassiljev. *Oil Fat Ind.* (Russia), 1928, No. 7, 9; *Chem. Centr.*, 1928, ii, 2417.

¹⁰ *Org. f. d. Öl- und Fetthdl.* 1913, Nos. 14 and 15, and *Seifen. Ztg.*, 1913, 529.

These hardened fish oils or other hardened oils put out under the trade names indicated have been manufactured by the Germania Oil Works of Emmerich.

3416. A species of hardened fish or whale oil, known as "Talgit," has been examined by Müller,¹¹ who found the product to have an acid value of 12.8, an iodine number of 49 and a titer (fatty acids) of 39.4° C. The fat was saponified and pressed to obtain stearic acid. It was found that the operation of pressing could be carried out effectively to yield a product technically free from liquid fatty acids; 35 per cent of solid fatty acid having a titer of 48.7° C. was thus obtained. Müller states that since mixtures of stearic and palmitic acids possess a solidifying point above 53.5° C. the low titer of the solid acids of Talgit points to the presence of solid acids other than stearic and palmitic. Dubovitz¹² thinks the low melting-point to be due to the presence in the original fish or whale oil of hypogaecic and physetoleic acid or similar acids with possibly unsaturated fatty acids of a still lower number of carbon atoms.

3417. Results obtained by Sandelin¹³ on the examination of hydrogenated products prepared from whale oil at a factory in Kaipiais, Finland, and also of hydrogenated whale oil, made in Germany and offered to a Finnish margarine factory, were:

	Melting-point	Solidifying-point °C	Refractometer Reading at 40° C.	Saponification Value	Acid Value
Original whale oil	fluid	fluid	64.1	192.2	9.50
Artificial tallow	47.5	38.1	48.9	183.7	9.88
Artificial stearine	54.3	47.3	32.4	187.7	7.80
Hydrogenated whale oil (German)	41.9	31.9	48.2	190.9	5.30

	Iodine Value (Wijs)	Reichert- Meissl Value	Polenske Value	Molecular Weight of Insoluble Acids	Melting- Point of the Ara- chidic Acid	Nickel Reac- tion
Original whale oil	144.8	0.27	0.69	287.7	—	—
Artificial tallow	56.9	0.25	0.49	296.4	75.5	+
Artificial stearine	11.7	0.14	0.31	297.0	74.1	+
Hydrogenated whale oil (German)	57.8	0.18	0.50	282.0	76.0	+

3418. Svendsen reports on the chemical composition of hardened whale oil. A sample of hardened whale oil had acid value 1.5, saponification value 195.7 iodine number 59.8, refractometer reading at 40° C., 50; it yielded no insoluble bromide. The fatty acids consisted of 10.8 per cent of myristic acid, 17.9 per

¹¹ *Seifen. Ztg.*, 1913, 1376.

¹² *Ibid.*, 1913, 1445.

¹³ *Teknikern*, 1913, 359; *Chem. Tech. Ber.*, 1914, 38,321; *J.S.C.I.*, 1914, 1097.

cent of palmitic acid, 10.6 per cent of Bull's C_{18} -acid, 10.8 per cent of stearic acid, 27.7 per cent of oleic acid, 3.4 per cent of arachidic acid, 8 per cent of a solid acid $C_{22}H_{42}O_2$, 2.5 per cent of behenic acid, and 8.8 per cent of an acid, $C_{22}H_{40}O_2$.¹⁴

3419. Aufrecht¹⁵ examined a number of hardened oils with the following results:

	1 Durotol (Yellow)	2 Durotol (White)	3 Hydrogenated Train Oil
Color	Yellowish	White	White
Specific gravity at 15° C.	0.9252	0.9257	0.9268
Melting-point, °C.	46.5	46.0	48.0
Solidification-point, °C.	43.5	43.5	45.5
Viscosity at 50° C.	5.4	5.4	5.6
Acid number (calculated as oleic acid)	0.51	0.57	0.83
Saponification number	162.2	161.0	173.5
Unsaponifiable matter (per cent)	1.92	2.1	2.4
Acetyl number	1.2	1.2	0.95
Iodine number	3.9	4.2	7.8
Hehner number	95.8	95.8	96.4
Reichert-Meissl number	0.38	0.36	0.52
Water	0.0	0.0	0.0
Ash	0.037	0.03	0.05

3420. Saponification Number: Unsaponifiable Matter. The saponification number practically does not change. The content of free fatty acids changes but little. A sample of cottonseed oil containing 1.8 per cent fatty acid was found, after hardening to various degrees, to have a fatty acid content ranging from 1.4 per cent to 1.9 per cent. With sesame oil containing 2.44 per cent fatty acid the resulting hardened oil contained 2.55 per cent of acid. The content of unsaponifiable bodies does not essentially change. Cottonseed oil having 0.55 per cent unsaponifiable matter, after hardening, showed an unsaponifiable content of 0.45 to 0.55 per cent, while sesame oil with 0.70, after hardening, had 0.85 per cent unsaponifiable.

3421. The sterols, according to Bömer, are not changed during hydrogenation of oils containing them,¹⁶ though they are readily hydrogenated in appropriate conditions.¹⁷

3422. An examination of the unsaponifiable constituents of several hardened oils has been made by Marcusson and Meyerheim,¹⁸ who used the digitonin method for the separation of sterol. The following table gives the results obtained:

¹⁴ *Tidskrift Kemi, Farm. Teraphi*, 1916, **20** 285; *J.S.C.I.*, 1917, 603.

¹⁵ *Pharm. Ztg.*, 1912, 876.

¹⁶ Cf. para. 3479.

¹⁷ See paragraphs 3461, 3464, also Chap. XXX, paragraph 3003, *et seq.*

¹⁸ *Zeitsch. f. angew. Chem.*, 1914, 27, 201.

UNSAAPONIFIABLE CONSTITUENTS OF HARDENED OILS

	Total Unsa- ponifi- able Matter	$[\alpha]_D$	Sterol Obtained by Digi- tonin Method	Sterol-Free Unsaponifi- able Components		
	Per Cent		Per Cent	Per Cent	$[\alpha]_D$	Iodine Number
Cottonseed oil (solidifying-point 32° C.) ...	0.7	- 5.8	0.22	0.4	+ 6.8
Cottonseed oil (solidifying-point 38° C.) ...	0.6	\pm 0	0.14	0.4	+ 8.1
Linseed oil	1.0	+19.5	0.21	0.7	+19	85
Castor oil	0.3	-10.1	0.13	0.19	+ 5.2
Talgol	0.9	- 1.9	0.10	0.7	+ 1.3	56.1
Talgol extra	0.9	- 3.3	0.07	0.7
Candelite	0.8	+ 4.7	0.05	0.7	+ 4.8
Candelite extra	0.7	+ 1.4	0.024	0.64	+ 2.8

3423. The examination showed that the sterol content of hardened fats is slightly less than that of the corresponding natural fat or oil. The cottonseed oil first listed was prepared by the Wilbuschewitsch process at 150° to 160° C. with hydrogen under pressure. The second sample of the cottonseed oil was made by the Normann process, presumably at a higher temperature but without pressure. At temperatures of 150° to 160° C. apparently the difficultly reducible sterol is not affected by hydrogen and Marcusson and Meyerheim call attention to the observations of Adamla¹⁹ who could not hydrogenate cholesterol with a nickel catalyzer at temperatures below 170° C. Marcusson and Meyerheim found cholesterol to hydrogenate readily at 195° C. while phytosterol was practically unchanged after treatment with hydrogen at 200° C. From these and other tests it was found that cholesterol is much less resistant than phytosterol to the action of hydrogen.

3424. The content of sterol decreases with increasing melting-point as shown by the following table:

Hydrogenated Oil	Iodine Number	Solidifying- point	Sterol Content
Whale oil (not hydrogenated)	114	0.13
Talgol	67	31	0.10
Talgol extra	36	38	0.07
Candelite	20	42	0.05
Candelite extra	13	45	0.02

3425. The unsaponifiable constituents of hardened fat when freed from sterols were of light yellow color and of salve-like consistency. These sterol-

¹⁹ *Dissertation*. Beiträge zur Kenntnis des Cholesterins, Freiburg, 1911, 12.

free bodies obtained from Talgol, Talgol extra, Candelite and Candelite extra, when recrystallized from benzine, yielded a product melting between 59.3° and 59.8°, which proved to be a fatty alcohol, probably octodecyl alcohol.

3426. Acetyl Number. In the case of the acetyl number more noticeable changes take place according to Normann and Hugel. When hardening castor oil, for example, the hydroxyl number in one sample dropped from 156 to 102; in another sample the number fell to 131. The hydroxyl group is thus more or less broken down by the hydrogenation process, at least under some conditions of treatment.

HYDROGENATED CASTOR OIL (GARTH)

Acid number.....	3.5
Saponification number.....	183.5
Iodine number.....	4.8
Acetyl number.....	153.5
Acetyl number of the fatty acids.....	143.1
Acid number of the fatty acids.....	184.5
Saponification number of the fatty acids.....	187.9
Melting-point of the fat.....	68° C.
Melting-point of the fatty acids.....	70° C.
Melting-point of the acetylated acids.....	47° C.

3427. The properties of hardened castor oil have been noted by Garth²⁰ whose observations differ somewhat from those of Normann and Hugel. As is generally known, castor oil differs materially from many other common oils in its solubility in alcohol and difficulty of salting out its soaps by electrolytes. The solubility in alcohol decreases with increasing hardness. When the hydroxyl group is completely hydrogenated the fat is, of course, no longer soluble in alcohol. Castor oil is miscible with gasoline only to a limited degree. With increase of hardening this peculiarity disappears.²¹ The constants of one sample of hardened castor oil examined by Garth are given in the above table.

3428. These results obtained by Garth indicate that the saponification and acetyl number did not change. The iodine number fell greatly and the melting-point was much increased. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones. As is known castor oil has the property at high temperatures of forming anhydrides, accompanied by polymerization.

3429. Color Reactions. The effect of hydrogenation on color tests of oils is variable. Thus the Baudouin sesame oil test is not influenced; in fact the reaction seemingly is sharper after treatment of the oil with hydrogen, while the Halphen test is not likely to give positive results even with oils which have been only slightly hardened.

3430. The Becci test is operative with slightly hardened cottonseed oil, but is indistinct with highly hardened oil so that this test is significant only in event of a positive coloration.

²⁰ *Seifen. Ztg.*, 1912, 1309.

²¹ See also para. 3341, page 347.

3431. Hardened fish oil loses all its essential characteristics, such as the formation of well-defined bromine compounds of the higher unsaturated fatty acids. Thus there are obtained after hardening, new fatty acids corresponding to the saturated bodies, arachidic ($C_{20}H_{40}O_2$) and behenic ($C_{22}H_{44}O_2$) acids, which in variable amounts up to a proportion of 20 per cent and more have been observed in certain hydrogenated oils. In the hardening of rape oil behenic acid is formed from the erucic acid present. Other oils or fats with a noticeable proportion of acids with more than 18 carbon atoms in the molecule apparently scarcely ever come into the trade.

3432. The complete conversion of erucic acid to behenic acid is readily obtained by reducing with hydrogen in the presence of nickel. This method has been used by Lewkowitsch in the determination of erucic acid.²²

3433. The saturated fatty acids obtained by the hydrogenation of the unsaturated acids of Japanese sardine oil were found by Majima and Okada²³ to have a melting-point of 75° C. and a molecular weight of 349, and consisted in the main of the higher homologs of stearic acid, such as $C_{20}H_{40}O_2$ or $C_{22}H_{44}O_2$.

3434. The glycerol content of hardened fats was determined by Normann and Hugel,²⁴ using several of the published methods, and the results obtained compared with those calculated from the ester values. The results obtained by the bichromate method agreed very well with the calculated values. Willstätter's method gave satisfactory results, but the results obtained by the acetin method were 1½ per cent lower than the calculated values.

3434A. Mackey Tests on Cottonseed Oil. Aspegren²⁵ finds that the tendency to spontaneous heating falls with the progressive disappearance of linoleic acid during hydrogenation.

II. DETECTION AND ESTIMATION OF HYDROGENATED OIL

3435. The methods used for the detection of hydrogenated oil are based on characteristics of the raw material and on changes produced during hydrogenation.

3436. Detection of Nickel. The detection of nickel in a suspected sample of fat raises an almost irrebuttable presumption that hydrogenated oil is present. A negative result does not exclude the possibility, first, because modern methods of hydrogenation using nickel catalyst and subsequent treatment of the hardened fat will sometimes yield a product in which nickel cannot be detected; secondly some other catalyst may have been used.²⁵

3437. Many methods have been worked out for the detection of traces of nickel in fats. Most of these methods depend on the use of dimethylglyoxime introduced by Tchugaeff.

²² Lewkowitsch, *Oils, Fats and Waxes*, 5th edition, Vol. 1, 195 and 553.

²³ *J.S.C.I.*, 1914, 362.

²⁴ *Chem. Umschau.*, 1916, **23**, 45.

²⁵ *Oil & Fat Ind.*, 1929, **6**, 19; *Brit. Chem. Abst.*, **1929**, 217A.

²⁶ On the natural occurrence of traces of nickel in foodstuff, see paragraphs 3446 and 3447.

3438. Kerr's method ²⁶ is intended for fats and oils and is highly practical. Ten grams of the fat to be tested are heated on the steam-bath with 10 cc. of hydrochloric acid (specific gravity 1.12), with frequent shaking for two to three hours. The fat is then removed by filtering through a wet filter paper, the filtrate being received in a white porcelain dish. The filtrate is evaporated to dryness on the steam bath, 2 to 3 cc. of concentrated nitric acid being added, after it has been partly evaporated, to insure the destruction of all organic matter. After the evaporation is complete the residue is dissolved in a few cubic centimeters of distilled water and a few drops of a 1 per cent solution of dimethylglyoxime in alcohol added. A few drops of dilute ammonia are then added. The presence of nickel is shown by the appearance of the red colored nickel dimethylglyoxime. The amount of nickel present may be estimated by comparing the color developed with that developed in a standard solution of a nickel salt.

3439. Lehmann ²⁷ reports the following results:

ASH OF HARDENED OIL

Oil	Milligrams per Kilo		
	Total Ash	Iron	Nickel
Peanut.....	2.3
Peanut.....	27.5	5.3	1.6
Peanut.....	40.0	6.3	6.1
Peanut.....	4.2
Peanut.....	5.0
Sesame.....	18.5	6.0	1.1
Sesame.....	23.0	4.2	1.1
Sesame.....	1.0
Cottonseed.....	23.5	3.9	0.07
Cottonseed.....	30.0	3.5	0.5
Cottonseed.....	0.4

The ash contained in addition very small amounts of aluminum, zinc and calcium.

3440. The detection of nickel in fats is carried out according to Schoenfeld by igniting 5 to 10 g. of the fat in a porcelain crucible. The ash is treated with 1 cc. of concentrated hydrochloric acid and heated on the water-bath, then dissolved in 2 to 3 cc. of water, filtered and the filtrate evaporated in a small porcelain dish. After moistening with a few drops of water a solution of dimethylglyoxime is added in the usual manner. Schoenfeld observed that far more certain results are obtained in this manner than by extracting the fat with hydrochloric acid, evaporating the hydrochloric acid solution and testing the residue for nickel. ²⁸

3441. The test for nickel involving extraction of the oil with hydrochloric acid, was not regarded by Prall as reliable under all conditions and he has found the following procedure to be more satisfactory: ²⁹

²⁶ *Ind. Eng. Chem.*, 1914, 207.

²⁷ *Chem. Ztg.*, 1914, 798.

²⁸ *Siefen. Ztg.*, 1914, 946.

²⁹ *Zeitsch. f. Unters. d. Nahrungs- u. Genussmittel*, 1912, 109.

One hundred to 200 g. of the fat are burned, little by little, in a platinum dish, and the residue is ignited. The ash is dissolved in 3 to 5 cc. acidulated water, containing 5 to 10 drops hydrochloric acid. The solution is heated somewhat to remove a considerable portion of the excess of acid and is then rendered alkaline with ammonia. On allowing to stand for one hour, iron and aluminum precipitate and are removed by filtration. The filtrate is evaporated to dryness in a small porcelain dish. The residue is moistened with ammonia and then a small amount of an alcoholic solution of dimethylglyoxime is added. Even with very small amounts of nickel (0.1–0.01 m.g. in 100 g. of fat) a distinct red coloration is apparent.

3442. Positive results are attained only by using at least 100 g. of the fat. The most convenient method of burning off the fatty matter is to heat the sample to the fire-point and allow the organic matter to quietly burn away. A blank test may be conducted by grinding nickel sulphate with oil and adding 1 cc. or 0.1 cc. (corresponding to 0.0002 g. or 0.00002 g., respectively of nickel) to 100 g. of oil, which is ignited and the residue tested as noted above.³⁰

3433. The Effect of Hydrogen on Oil Containing Dissolved Nickel. A sample of cottonseed oil which Ellis hardened with about 1 per cent of reduced nickel catalyzer was allowed to stand for two years in contact with the catalyzer. The hardened fat was then melted and the catalyzer removed by filtration. The filtered fat was distinctly green in color and on analysis was found to contain 0.04 per cent of nickel. A quantity of the filtered fat was subjected to a gradual increase of temperature, while a current of hydrogen was passed through the liquid fat. Portions removed at 145° C. and again at 160° C., still had a green tinge. At 170° C., the green color practically disappeared and at 185° C. no green color could be detected although the oil was apparently unblackened by formation of precipitated nickel.

3444. The detection and determination of small quantities of nickel by α -benzildioxime is described by Attack³¹ as follows: An alcoholic solution of α -benzildioxime gives with nickel compounds a bulky red precipitate which is insoluble in water, alcohol, acetone, 10 per cent acetic acid and ammonia; the precipitate becomes reddish yellow on boiling. The reagent is much more sensitive than dimethylglyoxime, showing 1 part of nickel in 5 million of water, and the precipitate is readily filtered. Small quantities of nickel are determined as follows: 150 cc. of a hot saturated alcoholic solution of the oxime are added for every 0.01 g. of nickel, the mixture is heated for a few minutes on the water-bath, filtered, the precipitate washed with hot alcohol, and dried at 110° to 112° C.; it has the formula $C_{12}H_{12}N_4O_4Ni$ and contains 10.93 per cent nickel. Nickel may be separated from cobalt in ammoniacal solution. α -Benzildioxime is prepared by boiling 10 g. of benzil, dissolved in 50 cc. of methyl alcohol, with a concentrated aqueous solution of 8 g. of hydroxylamine hydrochloride, for six hours, washing the precipitate with hot water and then with a small quantity of ethyl alcohol, in which it is only slightly soluble. It may be crystallized from acetone.

3445. According to Lindt, nickel may be determined colorimetrically by means of potassium thiocarbonate. Metals of the hydrogen sulphide group and manganese, cobalt and zinc should not be present.³²

3446. Natural Occurrence of Nickel in Animal and Vegetable Tissues. Certain tissue constituents of cardinal importance are present in scarcely detectable quantity. This has long been known to the biochemist, but the truth has recently been brought home to the laity by their familiarity with the vitamins. Among substances of apparently constant and possibly essential presence are metals.

³⁰ *Z. angew. Chem., Aufsatzteil*, 1915, 40.

³¹ *Chem. Ztg.*, 1913, 37, 773.

³² *J.S.C.I.*, 1914, 335.

Thus, zinc in minute traces is found in the gonads. Recently nickel has been discovered as an associate of insulin and there is a suspicion that the association may be functional. Several workers have reported the natural occurrence of nickel and cobalt in other animal and in vegetable tissues. Bertrand and Mâcheboeuf found 0.09 mg. nickel in human liver and 0.022 mg. in the brain, per kilogram of organ weight. Nickel was also detected in tissues of the bull, fowls, fish, lobster, molluscs and tunicates. In the mussel 0.455 mg. of nickel per kilo was present. Cobalt was often present but no quantitative work was done on this metal.²³

3447. Bertrand and Mokrgatz²⁴ examined twenty-three vegetables and found nickel and cobalt in all, nickel being present in larger quantity. The nickel was present in amounts from 0.01 mg. in the tomato to 2.0 mg. in the pea, while cobalt ranged from 0.003 mg. in the carrot to 0.3 mg. in the lentil, all per kilogram of fresh material.

3448. *Detection of Iso-oleic Acid.* The method of Twitchell, already described in paragraph 3304, is the best for the identification and estimation of iso-oleic acid. The presence of iso-oleic acid in beef fat in small quantity reported by Twitchell (*loc. cit.*) seems to be an isolated observation: one wonders whether the specimen was authentic or whether some hydrogenated fat had been present in feed cake eaten by the animal. Apart from this one anomalous instance, the possession of more than a fractional iodine number by the solid fatty acids separated by the Twitchell method may be taken as evidence of the presence of hydrogenated oil.

3449. Formerly²⁵ an attempt would be made, by collating the quantity of iso-oleic acid found with other quantitative characters of a fat, to estimate, approximately, the percentage of hydrogenated oil present. Owing to the introduction of processes with low hydrogenating temperatures this would now be practicable only if the hardened oil and its method of manufacture were known. Otherwise, the estimation of iso-oleic acid must be regarded as little more than a method for *detecting* hydrogenated oil. If a high percentage of iso-oleic acid is found, e.g., 30-40 per cent, the fat is probably composed almost entirely of hydrogenated oil which has been hardened at a high temperature.

3450. Klimont and Mayer²⁶ propose the following test for hydrogenated oil in butter substitute: 2 to 3 g. of the sample is melted, and dissolved in acetone to a total volume of 50 cc. After standing for twelve hours at the ordinary temperature, the crystals which separate then are filtered off, dried and weighed. Oleomargarine yields 12 to 13 per cent of crystals of m.p. 45° to 47° C. In the case of artificial mixtures of oleomargarine with hydrogenated fish oil and rape oil, the portion crystallizing from acetone was, in all cases, considerably greater than 12 to 16 per cent, which may be taken as the limits for genuine oleomargarine. It was possible by this test to detect 3.5 per cent of hardened fish oil when this was added, together with 5.5 per cent of rape oil, to oleomargarine.

²³ *Compt. rend.*, 1925, **180**, 1380. For physiological rôle and pharmacology of nickel and cobalt consult Bertand and Nakamura, *Compt. rend.*, 1927, **185**, 321 and Mascherpa, *Arch. exp. Path. Pharm.*, 1927, **124**, 356; *Brit. Chem. Abst.*, 1927, 992A; Yamagami, *Folia pharmacol.*, Japan, 1928, **6**, 389; *Chem. Abst.*, 1929, **23**, 2216.

²⁴ *Bull. Soc. chim.*, 1925, iv, **37**, 554; *Science*, 1929, **69**, May 24, p. 12, refers to similar work by Kaufmann and Keller.

²⁵ Cf. Williams and Bolton, *Analyst*, 1924, **49**, 464.

²⁶ *Z. angew. Chem.*, 1914, **27**, 645; *J.S.C.I.*, 1915, 148.

3451. Gerritzen and Kauffmann ³⁷ seek to detect the presence of hardened oil in tallow by means of the iodine number of the solid fatty acids separated by Twitchell's method (see para. 3304, this volume). The iodine value of the fatty acids separated from beef fat by the Twitchell method, is always below 6; a higher iodine value indicates admixture, either with mutton fat, for which the corresponding value may be as high as 13, or with hardened vegetable oils, for which, owing to the presence of iso-oleic acid (see para. 3300) and related acids, the corresponding value may be as high as 27. If there has been no admixture with mutton fat the percentage of hardened vegetable oil in a commercial beef fat may be calculated with fair accuracy from the iodine value of the separated fatty acids.³⁸

3452. Detection of Arachidic Acid. As a test for hydrogenated peanut oil, Kreiss and Roth ³⁹ have given a method which consists in saponifying 20 g. of the oil with 40 cc. of alcoholic potash; then adding 60 cc. of alcohol and acidifying by the addition of 50 per cent acetic acid of which approximately 15 cc. are required. One and one-half grams of lead acetate are added and the mixture allowed to stand overnight. The lead salts which separate are decomposed by boiling with 5 per cent hydrochloric acid, the fatty acids are dissolved in 50 cc. of 90 per cent alcohol with slight warming and the solution is placed in water at 15 degrees for about one-half hour. The crystals which separate are recrystallized from 25 cc., then 12½ cc. of 90 per cent alcohol and the melting-point determined. The presence of at least 5 per cent arachidic acid causes the melting-point of the third crystallization to be over 70° C.

3453. Normann and Hugel ⁴⁰ state that this test is applicable likewise to hardened fish and rape oil. They tested a number of samples of fish oil from several sources and found in each case that the melting-point of the recrystallized fatty acids was at least 70° C. Normann and Hugel also state that it is unnecessary with hardened fish oil to allow the lead acetate to react for several hours, it sufficing simply to let the mixture stand until cooled to room temperature; this can be hastened by cooling with water. So large a proportion of fatty acids is obtained according to this procedure that the specified amount of alcohol is not sufficient to dissolve them. It is better to use 100 to 150 cc. of alcohol and heat on the water-bath until solution is effected. The application of heat should not be continued for any great length of time as arachidic acid readily forms esters. The mixture is then placed in cold water, cooled to room temperature and the separated material collected and crystallized several times from alcohol used in progressively diminishing proportions. Three crystallizations suffice for only slightly hardened fats. With fats of higher consistency one must recrystallize several times more until the melting-point is constant.

3454. In one case using hardened fish oil having a melting-point of 44°, three recrystallizations from alcohol gave a constant melting-point of only 63°, while

³⁷ *Chem. Weekblad.*, 1927, **24**, 554.

³⁸ *Brit. Chem. Abst.*, **1927**, 944B.

³⁹ *Chem. Ztg.*, 1913, 58 and 369.

⁴⁰ *Ibid.*, 1913, 815.

further recrystallization using acetone caused the melting-point to advance to 76°. In doubtful cases one should try several solvent mediums. If the melting-point is found to be above 70° C. Normann and Hugel think it proof that either hardened fish, rape or peanut oil is present.

3455. In the identification of hardened marine oils and rape oil, Normann and Hugel supplement the usual melting-point test for arachidic acid by the determination of the saponification value of the fatty acids, using an excess of alkali and titrating back the excess. A direct determination with N/10 alkali is uncertain.⁴¹

3456. The hydrogenation process is used by Biazzo and Vigdorcik⁴² as a means of determining colza or rape oil in olive oil. The procedure is based on the transformation of erucic into behenic acid, using palladium as catalyzer. Behenic acid is characterized by slight solubility in 90 per cent alcohol, by high melting-point (84°) and by its quantitative yield from erucic acid. The catalyst was that of Mannich and Thiele⁴³ made by depositing reduced palladium upon ignited animal charcoal, giving a catalyzer that will saturate fatty substances completely, using 1 part palladium to 15,000 parts oil.

3457. Biazzo and Vigdorcik's method is as follows; Saponify 20 g. of the oil and extract fatty acids with ether and sulphuric acid. Dry the ether extract with calcium chloride, distil off the solvent and remove the last traces from the residue by placing in hot oven for fifteen minutes and blowing a current of air over it from time to time. Dissolve the acids obtained in 180 cc. anhydrous acetone, warm on the water-bath to incipient boiling, add 20 cc. N caustic potash and cool to 15°. Collect the precipitated fatty acids by use of the pump, wash with 4 portions of 10 cc. cold acetone, finally dissolve in water and extract from the solution the solid fatty acids with hydrochloric acid and 100 cc. ether. Wash the ethereal extract twice, each time with 100 cc. water and then shake for five minutes with 15 cc. 30 per cent aqueous solution of lead acetate, subsequently removing the supernatant aqueous layer. Filter the precipitate "A" of lead soaps from the ethereal solution "B," first allowing the liquid, if necessary, to stand on a bath at 23° to 25° for one-half hour. Examine the precipitate "A" for arachidic and lignoceric acids, i.e., for peanut oil. Free solution "B" from lead by use of hydrochloric acid and wash till the mineral acid is completely removed. Hydrogenate by palladium catalyzer till hydrogen is no longer adsorbed, filter and evaporate the solvent. Treat the residue by fractional crystallization as in the method of separating arachidic and lignoceric acids. If the final crystallization gives a substance with melting-point above 71°, the oil under examination contains a cruciferous oil. Positive indications are furnished by a melting-point between 76° to 79°. The sensitiveness of the method depends upon the care employed in preparing the palladium catalyzer, and in collecting and washing the acid potassium soaps, insoluble in acetone, at 15°.

3458. Bömer's "Difference Number."⁴⁴ Fifty grams clear filtered fat is dissolved in 50 cc. ether and allowed to stand, covered, for one hour at 15° C., with frequent stirring. Filter with suction: press the crystals. Dissolve in 50 cc. ether and repeat. Repeat all until glycerides melt at 61°–65° C. For very soft fats work at 5° C. and wait two hours for crystallization. Reduce 0.1–0.2 g. to a powder and set aside one half for melting-point determination. Saponify the other half by boiling for five minutes with 10 cc. half-normal alcoholic KOH. Dilute with 100 cc. water, place in separatory funnel, add 2–3 cc. 25 per cent

⁴¹ *Chem. Umschau.*, 1916, **23**, 131; *J.C.S.I.*, 1917, 658; *Chem. Abst.*, 1917, 2736.

⁴² *Ann. Chim. applicata*, 1916, **6**, 185–195; *J.S.C.I.*, 1917, 90; *Chem. Abst.*, 1917, 713.

⁴³ *Chem. Abst.*, 1918, **10**, 2158.

⁴⁴ *Z. Unters. Nahr. Genussm.*, 1914, **26**, 559; *Chem. Abst.*, 1914, **8**, 1174.

HCl, shake with 25 cc. ether, wash the ether twice with 25-cc. portions of water, filter through dry filter into a dish, boil off the ether and dry the fatty acids for one hour at 100° C. Cool, reduce to a powder. Determine the melting-point *at once*, simultaneously with that of the glycerides, by the capillary tube method. The difference in the melting-points is the Bömer difference number. According to Gronover and Blechschmidt ⁴⁵ this method is suitable for the detection of hydrogenated train oil in lard.

3459. An investigation of this Bömer difference number method, which was originally intended for the detection of tallow in lard, made by Prescher ⁴⁶ led to the examination of fifty-eight fats by both this method and by the Polenske ⁴⁷ method.

In the case of 25 samples of adulterated lard only 3, containing, respectively, 10, 30 and 30 per cent of beef tallow, could be detected by the Polenske method, the others, some containing as much as 15 per cent of beef tallow, giving negative tests. The Bömer method failed in only two cases, in which 5 and 10 per cent, respectively, of beef tallow were present. Eighteen samples of pure lard gave negative tests by the Bömer method, the Polenske procedure giving false indications of adulterations in two cases. Hydrogenated vegetable oils give a positive Bömer test and can also be distinguished from beef tallow by the phytosterol acetate test.

3460. Unsaponifiable Matter. Examination of the unsaponifiable matter has been suggested and used as a test for detecting animal fat in vegetable fats and *vice versa*. The first procedure involves a quantitative determination of the unsaponifiable matter. The method of doing this is fully described in manuals of oil analysis.⁴⁸ According to Wittka ⁴⁹ this estimation serves especially well for the detection of additions, whether of animal or vegetable origin, to beef fat. He observes that whereas beef tallow and its products normally contain 0.27 per cent of unsaponifiable matter, and at most 0.35 per cent, the animal and vegetable oils usually used for hardening purposes, as rape, sesame, linseed, soya, whale, seal, sardine, and herring oils, have much higher values varying between 0.75 and 1.40 per cent (castor oil is an exception with a value of 0.2 per cent). Since these figures remain substantially the same after the oils are hardened, the determination of unsaponifiable matter affords a direct test for the presence of hardened fats.⁵⁰

3461. In 1891 Bömer introduced the phytosterol acetate test as a means of detecting the addition of cheap vegetable fats to the more expensive animal fats. The test (which is by no means simple in technique) depends on the isolation from the unsaponifiable matter of a phytosterol (vegetable sterol) which, on acetylation, gave an acetyl compound with a melting-point of 125° C. or higher. In 1891 only one cholesterol (animal sterol) was known and that gave an acetate melting at 114°–115° C. Since then, however, at least two animal sterols have been discovered whose acetates melt at 129° C. and at 134° C. Fortunately they

⁴⁵ *Z. Untersuch. Lebensm.*, 1927, **53**, 250; *Chem. Abst.*, 1927, **21**, 3398.

⁴⁶ *Z. Unters. Nahr. Genussm.*, 1917, **29**, 433.

⁴⁷ *Chem. Abst.*, 1908, **2**, 716.

⁴⁸ Lewkowitsch, *Oils, Fats and Waxes*, 5th ed.

⁴⁹ *Chem. Umschau.*, 1927, **34**, 295.

⁵⁰ *Brit. Chem. Abst.*, 1927, 944B.

are found in substances (chrysalis oil and wool-fat respectively) not often used as adulterants of animal fats. Therefore, the phytosterol acetate test may still be useful to detect the presence of vegetable oils and fats in animal fats and, if the sterol undergoes no change in the conditions of industrial hydrogenation, it is available for the detection of hardened vegetable oil.⁵¹ For a discussion of the value of the test and for details of the technique the reader is referred to an article by Allan and Moore (*J.S.C.I.*, 1927, 433T).

3462. According to Sprinkmeyer and Diedrichs⁵² the quantity of phytosterol obtained from oils is reduced by hydrogenation.

3463. A report on fats and oils by Kerr⁵³ affords a study of two methods for the detection of phytosterol in mixtures of animal and vegetable fats: (1) Bureau of Animal Industry method⁵⁴ and (2) the digitonin method of Marcusson and Schilling.⁵⁵

Three samples were sent out: (1) Lard containing 5 per cent cottonseed oil and 0.25 per cent vaseline. This amount of vaseline would effectually prevent accurate observations by the present provisional method. (2) Pure lard, rancid. Rancidity interferes decidedly with the present method. (3) Lard containing 2.5 per cent hydrogenated cottonseed oil and 2.5 per cent soya-bean oil. Three collaborators were led to correct conclusions by each method. The digitonin method is more simple and convenient but the reagent is expensive and difficult to obtain. The Bureau of Animal Industry method requires more time and labor in manipulation but does not depend on an expensive reagent. Both methods are decidedly superior to the present provisional method and are recommended for adoption by the Association as provisional methods.

3464. The effect of hydrogenation on cholesterol and phytosterol has been investigated by Marcusson and Meyerheim,⁵⁶ with the following results.

Cholesterol and phytosterol were separated from the unsaponifiable matter of natural and hydrogenated oils and fats by the digitonin method of Windaus.⁵⁷ The amounts found in natural fats ranged from 0.03 (tallow to 0.38 per cent (linseed oil). Calculated on the unsaponifiable matter the proportion ranged from 33 to 55 per cent in the case of the vegetable oils examined, and from 8 to 14 per cent in the case of the animal fats (cod-liver oil and tallow). In addition to phytosterol or cholesterol other alcohols are present in the unsaponifiable matter, which either neutralize the optical laevorotation (as in the case of cottonseed oil) or even produce dextrorotation (linseed, cod-liver, and especially sesame oil). The presence of sesamol affords a means of detecting sesame oil, when no color reactions can be obtained. The unsaponifiable matter left after separation of cholesterol or phytosterol was a thick oil or semi-solid mass consisting in the main of unsaturated dextrorotatory alcohols (laevorotatory in the case of ox tallow) and small quantities of hydrocarbons. Only in the unsaponifiable matter of dark cod-liver oil were considerable amounts of hydrocarbons found. The dextrorotatory power of the unsaponifiable matter of sesame oil was greatly increased by the removal of the phytosterol. The iodine value (Hübl-Waller) of the residual unsaponifiable matter ranged from 56 to 78. As a rule hydrogenated fats contained less cholesterol or phytosterol than the corresponding natural fats, and the proportion decreased with the

⁵¹ For hydrogenation of sterols see paragraphs 3421, 3464, also Chap. XXX, paragraph 3003 *et seq.*

⁵² *Z. Unters. Nahr. Genussm.*, 1914, 236; *Chem. Abst.*, 1915, 940.

⁵³ *J. Assoc. Off. Agr. Chemists*, 1915, 1, 313.

⁵⁴ *U. S. Bur. Animal. Ind.*, Circ. 212.

⁵⁵ *Chem. Abst.*, 1914, 8, 1022.

⁵⁶ *Mitt. k. Materialprüf.*, 1916, 33, 221-225; *J.S.C.I.*, 1916, 549; *Seifen. Ztg.*, 1916, 168. See also Willstätter and Meyer. *Ber.* 41, 2199; Diels and Abderhalden, *Ber.* 39, 884, and Moreschi, *Rend. soc. chim. Ital.*, 1914 (2), 5, 236.

⁵⁷ *J.S.C.I.*, 1915, 1152.

degree of hydrogenation. For example, the following results were obtained in the progressive hydrogenation of a marine animal oil:

	Iodine Value	Solidifying-point, Degrees C.	Cholesterol, Per Cent
Original marine animal oil.....	114	0.13
Talgol.....	67	31	0.10
Talgol extra.....	36	38	0.07
Candelite.....	20	42	0.05
Candelite extra.....	13	45	0.02

3465. The unsaponifiable matter of hydrogenated fats after removal of the cholesterol or phytosterol was a yellow semi-solid mass, from which, in the case of Talgol, and Candelite, a saturated alcohol, m.p. 59.3° to 59.8° C. could be extracted with petroleum spirit. It had a refractive index of 1.4268 at 100° C. and appeared to be octodecyl alcohol. Transformation products of cholesterol were not obtained from Talgol or Candelite, but derivatives of phytosterol could be separated from hydrogenated vegetable oils. For example, repeated recrystallization of the unsaponifiable matter of hydrogenated linseed oil from 96 per cent alcohol yielded an alcohol (m.p. 75° C.) which did not give the characteristic phytosterol reactions.

3466. Hydrogenated marine animal oils may be detected according to Marcussen and Huber⁵⁸ by an examination of the unsaponifiable matter for the presence of octodecyl alcohol, m.p. 60°.

3467. A specific reaction of marine animal oils and their hydrogenation products is described by Tortelli and Jaffe.⁵⁹ The reaction depends upon the fact that these oils contain a chromogenic compound which remains unaltered even in the hydrogenation process, and towards which bromine, the reagent used, plays the part of an auxochrome, forming a coloring matter that tints with a beautiful green a chloroform solution of the oil tested.

3468. The procedure is as follows: Into a graduated cylinder (with foot) provided with ground-glass stopper, and 15 mm. in diameter and 15-cc. capacity, are put 1 cc. of the oil, 6 cc. chloroform and 1 cc. glacial acetic acid. The liquid is agitated until it is homogeneous, when 40 drops of a 10 per cent chloroform solution of bromine are added, the whole is again strongly agitated for a moment and the cylinder placed upon a sheet of paper. If the oil in question belongs to the group of marine animal oils it will assume within a minute a fugitive pink followed by a bright green color, becoming more and more clear and intense, and remaining so for over an hour, after which the color turns to brown or sepia. The test is sharper as the oil is more purified or refined. Vegetable oils, tested as above, remain uncolored, or at most take on a clear yellow, which does not change within an hour, then becoming orange or dull yellow. Hemp oil, however, becomes green before addition of bromine and then passes decidedly into yellow. Oils of terrestrial animals take quickly a yellowish color, which in the course of an hour always darkens to brown or sepia. Hydrogenated fats are tested as follows: A larger cylinder is used (30 mm. in diameter and about 25 cc. in capacity), into which are introduced 5 cc. of the melted fat, 10 cc. chloroform, and 1 cc. acetic acid; after agitating well, add 2.5 cc. of 10 per cent chloroform solution of bromine and agitate again. There appears almost immediately a fugitive yellowish pink, which changes in a minute to a bright green, then quickly to an intense green, lasting over an hour. Many tests were made by Tortelli and Jaffe with different oils and fats, and the color reactions were always positive. Five per cent of hydrogenated fish oil in various edible fats has been detected by this test.⁶⁰

⁵⁸ *Mitt. k. Materialprüf.*, **34**, 54.

⁵⁹ *Ann. chim. applicata*, **2**, 80-98; *Chem. Abst.*, 1914, 3723; *J.S.C.I.*, 1914, 1061.

⁶⁰ *Chem. Ztg.*, 1915, 14.

3469. The reliability of this color reaction is questioned by Grün and Janko.⁶¹ Tests for hydrogenated fish and whale oil made according to Tortelli and Jaffe do not give good results with thoroughly hardened fats, but the color reaction is shown when incompletely hydrogenated products are used.⁶² The results obtained by the author confirm this view.

3470. The bromine reaction of Tortelli and Jaffe is stated by Davidsohn⁶³ to be of little value for the detection of marine animal oils, for many of such oils fail to give a green coloration in the test.

3471. Hydrogenation products of marine animal oils give an intense green color, but so also do hydrogenized vegetable oils, such as linseed oil and soya-bean oil. The octobromide test of Marcusson and Huber fails with marine animal oils which have been hydrogenated or strongly heated, but is to be preferred to Tortelli and Jaffe's test, because its indications are trustworthy when a positive result is obtained.

3472. Tsujimoto⁶⁴ advises that most marine animal oils give the Tortelli-Jaffe color reaction⁶⁵ especially when the oils are fresh. Old and inferior samples, however, give no coloration, or the coloration obtained is indistinct. In some cases, the coloration is given by old oils after these have been refined. The mixed fatty acids of marine animal oils as well as their distillates give the coloration, but the unsaponifiable matters and higher unsaturated fatty acids do not enter into the reaction. Hydrogenated fish oils give indistinct colorations with the test; vegetable oils and terrestrial animal oils and fats do not give a reaction.

3473. Hydrogenated marine animal oils are indicated according to Prescher by the color reactions of Tortelli and Jaffe, together with positive results in Kriess and Roth's test for arachidic acid and the cholesterol acetate test.

The presence of arachidic acid and a positive result in the phytosterol acetate test indicate peanut or rape-seed oils. Sesame oil is detected by the Soltsien and Baudouin tests. An excessively low saponification value points to rape oil, while cocoanut and palm-kernel oils are indicated by saponification values exceeding 230 and by the Reichert-Meißl and Polenske values. Hydrogenated castor oil has a high hydroxyl value, while hydrogenated cottonseed oil may be detected by Becchi's and Hauchecorne's tests. The ratio between the iodine value and refractive index is different in hydrogenated fats from the ratio in animal fats. Cocoanut oil is distinguished by its very low iodine value. Bellier's reaction is only applicable to a limited extent to the detection of hydrogenated vegetable oils. The dimethylglyoxime test for nickel may also be inconclusive, since many freshly expressed oils give a red coloration in the absence of nickel.⁶⁶

3474. Response to Halphen Test. Hydrogenated cottonseed oil was first stated by Paal and Roth to give no coloration when subjected to the characteristic Halphen test and the same statement has been made by later investigators. The amount of hydrogenation which is required to render the oil just incapable of responding to the test was investigated by Moore, Richter and Van Arsdel. To determine that point a quantity of oil was hydrogenated at a temperature of 150° to 160° C., 2 per cent nickel on a carrier acting as catalyzer. Samples were taken (a) of the original oil, (b) of the mixed oil and catalyzer before heating, (c) of the mixed oil and catalyzer when heated to 150° C., five minutes being required to reach this temperature, (d) after three-minute hydrogenation, (e) after nine-minute hydrogenation, and (f) after fifteen-minute hydrogenation. A similar sample of oil was heated to 150° to 160°

⁶¹ *Seifenfabrikant*, 1915, 253-255.

⁶² *Seifen. Ztg.*, 1915, 374.

⁶³ *Seifen. Ztg.*, 1915, 42, 657 and 678; *Z. angew. Chem.*, 1915, **28**, Ref., 560; *J.S.C.I.*, 1916, 186.

⁶⁴ *J. Chem. Ind., Japan*, 1915, **18**, 1368; *J.S.C.I.*, 1916, 262.

⁶⁵ *J.S.C.I.*, 1914, 1061.

⁶⁶ *Z. Unters. Nahr. Genussm.*, 1915, **30**, 357; *Z. angew. Chem.*, 1916, **29**, Ref. 165; *J.S.C.I.*, 1916, 548.

for twenty minutes in the absence of any hydrogen or catalyzer, and was then found to give the same intensity of Halphen test as Sample *a*. The other samples gave tests as follows:

Sample	Iodine Number	Result
<i>b</i>	104.9	Not noticeably diminished.
<i>c</i>	103.7	Distinctly weaker test.
<i>d</i>	102.7	Faint test in three minutes.
<i>e</i>	101.3	Faint test after heating one and one-half hours.
<i>f</i>	97.6	Negative even after heating one and one-half hours.

A drop of four units in iodine number may be said to have destroyed the chromogenetic substance.

3475. An attempt is made by Grimme⁶⁷ to identify marine animal oils by color reactions after they have been hardened. A list of tests is given for each of the four classes of marine animal oils: (1) Seal oils; (2) Whale oils; (3) Liver oils; (4) Fish oils; and also characteristic tests for individual oils. These tests were also applied to two hardened oils of unknown origin and Grimme believes from his results that the color reactions are characteristic enough to establish the presence of marine animal oils. Nickel was found in the samples, Fortini's test (as detailed below) giving the strongest coloration. Color reactions were applied to six authentic whale oils from two different sources, and hardened to different degrees. These tests were carried out by dissolving 5 parts of the sample in 95 parts of benzene-xylene (1 : 1) and agitating 5 cc. of the solution with the reagent; after five minutes and sixty minutes the color was noted. Grimme finds the iodine-sulphuric acid reaction (1 cc. concentrated sulphuric acid and 1 drop tincture of iodine) to give a characteristic violet-red color for whale oil though the intensity of coloration decreases with increasing hardness. The constants of the six samples of hydrogenated fish and whale oils employed and the coloration produced by different reagents are tabulated by Grimme.

3475A. CONSTANTS OF HYDROGENATED FISH AND WHALE OILS

Sample	Consistency	Specific Gravity	Melting Point, Degrees C.	Solidifying-point, Degrees C.	Index of Refraction	Acid Number	Acid Number as Free Oleic Acid, Per Cent	Saponification Number	Iodine Number (Wijs)
I.....	Lard-like	0.9256	38.5	32.8	1.4569	3.72	1.91	188.8	56.76
II.....	Tallowy	0.9259	40.0	35.2	1.4548	8.49	4.26	189.8	49.82
III.....	Tallowy	0.9258	42.4	36.4	1.4543	5.64	2.90	189.6	41.36
IV.....	Tallowy	0.9263	44.8	39.3	1.4539	4.39	2.21	189.2	35.71
V.....	Tallowy	0.9271	47.2	41.5	1.4536	4.40	2.25	188.7	26.95
VI.....	Tallowy	0.9271	48.0	42.0	1.4530	2.18	1.10	189.3	23.18

⁶⁷ *Chem. Rev. u. d. Fett und Harz Ind.*, 1913, 129 and 155.

COLOR REACTIONS (GRIMME)

3475B.

Reagent	Color of Layers	I	II	III	IV	V	VI
1 cc. concentrated sulphuric acid.....	Acid Fat solution	Brown Yellow	Cherry-red Yellow	Cherry-red Light-yellow	Yellow Light-yellow	Yellow Colorless	Yellow Colorless
1 cc. 70 per cent sulphuric acid.....	Acid Fat solution	Light-brown	Light-brown	Light-brown	Yellow	Yellow	Yellow
1 cc. 20 per cent sulphuric acid.....	Acid Fat solution	Rose	Rose	Light-rose	Light-rose	Faint-rose	Colorless
1 cc. acetic anhydride, then 10 drops of concentrated sulphuric acid.....	Acid Fat solution	Dark-brown Grayish-green	Brown Grayish-green	Brown Grayish-green	Brown Grayish-yellow	Light-brown Grayish-yellow	Light-brown Grayish-yellow
1 cc. mixture equal parts concentrated sulphuric acid and fuming nitric acid.....	Acid Fat solution	Red-brown Yellow	Red-brown Yellow	Brown Yellow	Brown Yellow	Light-brown Yellow	Light-brown Yellow
Diluted with water after $\frac{1}{2}$ hour.....	Acid Fat solution	Yellow	Yellow	Bright-yellow	Bright-yellow	Bright yellow	Bright-yellow
5 drops concentrated sulphuric acid saturated in the cold with bichromate; after 5 minutes 5 cc. water.....	Acid Fat solution	Yellow Brownish-black	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown
10 drops fuming nitric acid.....	Emulsion Acid	Brownish-red	Brownish-red	Brownish-red	Brownish-red	Brownish-red	Brownish-red
Diluted with water after $\frac{1}{2}$ hour.....	Fat solution	Light-brown then yellow	Light-brown then yellow	Light-brown then yellow	Yellow	Yellow	Yellow
10 drops aqua regia.....	Acid Fat solution	Brownish-yellow	Brownish-yellow	Brownish-yellow	Brownish-yellow	Brownish-yellow	Brownish-yellow
Diluted with water after $\frac{1}{2}$ hour.....	Acid Fat solution	Brownish-yellow	Brownish-yellow	Brownish-yellow	Brownish-yellow	Brownish-yellow	Brownish-yellow
1 cc. concentrated sulphuric acid and one drop tincture of iodine.....	Acid Fat solution	Violet-red	Violet-red	Violet-red	Violet-red	Violet-red	Violet-red

3476. A simple method for the detection of tallow and hydrogenated fats in butter fat is proposed by Amberger.⁶⁸ The procedure is based upon the relative insolubility in ether of tristearin and β -palmitodistearin as compared to the other glycerides.

Pure butter fat when dissolved in a certain proportion of ether forms a solution which deposits no crystals when kept for a definite time at a certain temperature. Under these conditions the presence of foreign fats containing tristearin or β -palmitodistearin is shown by the separation of crystals. The method recommended is as follows: Weigh 31 g. of the clear melted (40° to 50°) fat into a 100-cc. volumetric flask. Fill the flask to the mark with ether and cool in a water-bath at 15°. Mix well and add sufficient ether to bring the level of the liquid to the mark. After letting stand for one hour in the bath again thoroughly shake the mixture. Repeat the shaking after another hour. If only a trace or no deposit has formed in the mixture the butter is pure or it contains less than 12 per cent of tallow. If crystals have formed filter the mixture by means of suction through a paper disc placed upon a perforated porcelain plate, transferring the crystals remaining in the flask by means of 3.4 cc. of ether containing 20 per cent alcohol. Cover the funnel containing the perforated plate and continue the suction until the crystals are drained free of liquid. Transfer the crystals to a tared watch-glass by means of a spatula and allow them to dry at room temperature or heat until melted to remove the solvent. If the glycerides recovered in this manner weigh 0.4 g. or over, 15 per cent or more of tallow or hydrogenated fat is present. A considerable number of analyses are given illustrating the value and limits of the method. In case the hydrogenation process has been very incomplete (iodine number reduced less than half), the product cannot be detected by this method, but in other cases their detection is relatively certain. The addition of 15 per cent of tallow to butter fat gave 0.96 to 1.40 g. of crystallized glycerides and larger proportions yielded correspondingly greater amounts.

3477. To detect the presence of hydrogenated oil in butter fat Seidenberg⁶⁹ makes use of the turbidity point produced by cooling a solution of the fat in ether-alcohol. The results obtained with three samples of hydrogenated oils differed considerably, depending upon the degree of hydrogenation. The iodine numbers of these fats were determined and found to be as follows: No. 1, 73.4; No. 2, 34.5; and No. 3, 3.4. In No. 1, the amount of the saturated and less soluble glycerides is comparatively small, so that these latter do not raise the turbidity point of butter fat sufficiently to serve for their detection. The effect of the saturated glyceride produced by the hydrogenation is also seen in a comparison of the results between hydrogenated fats Nos. 2 and 3. In the case of No. 3, having an iodine number of 3.4, the addition of even 5 per cent can be detected with certainty, while No. 2, which has an iodine number of 34.5, can be detected in quantities of 10 per cent or above.

3478. Brauer⁷⁰ draws attention to the ability of hardened fats to hold water in suspension. Samples of hardened and other fats used in the manufacture of margarine were melted and agitated with water and the percentage of water in the emulsion determined both before and after the removal of as much as possible by pressing. The following figures were obtained: Hardened whale oil, 89 per cent, 23 per cent; hardened soya-bean oil, 25 per cent, 7 per cent; hardened herring oil, 18.6 per cent, 9.9 per cent; hardened linseed oil 96 per cent, 5.8 per cent; cocoanut oil, 6.4 per cent, 3.6 per cent; tallow, 15 per cent, 10.8 per cent.

⁶⁸ *Z. Unters. Nahr. Genussm.*, 1916, **31**, 297; *Chem. Abst.*, 1917, 1695; *J.S.C.I.*, 1916, 1077.

⁶⁹ *J. Ind. Chem.*, 1918, 617.

⁷⁰ *Chem. Zeit.*, 1922, **46**, 793-794; *J.S.C.I.*, 1922, **41**, 769A.

The striking ability of hardened whale oil to take up water and retain it even after pressing is suggested as a means of distinguishing between it and other hard fats.

3479. Effect of Hydrogenation on Vitamins. Although commercial hardened oils appear to lose their vitamins in manufacture, evidence is accumulating that this is not due to hydrogenation, *per se*, but to other conditions, such as high temperature and oxygen. Dubin and Funk ⁷¹ have gone into the question of the effect of exhaustive hydrogenation of cod-liver oil and appear to have established that vitamins A and D are unaffected by the treatment. Evans and Burr ⁷² have shown that wheat-germ oil may be hydrogenated in presence of palladium at 75° C., without injury to vitamin E.

⁷¹ *Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 1390.

⁷² *Proc. Nat. Acad. Sci.*, 1925, **11**, 334.

CHAPTER XXXV

APPARATUS FOR THE INDUSTRIAL HYDROGENATION OF FATTY OILS

3500. In the second edition of this book much space was taken up by the description, in some detail, of the various complicated types of apparatus that had been proposed for the commercial hydrogenation of fatty oils. Most of these enjoyed but a short life; not a few were still-born. The appliances in actual use are, for the most part, of great simplicity. In this edition, therefore, much of this detailed description is omitted. It has not, however, been deemed wise to eliminate such matter altogether. The use of hydrogenation in industries other than oil-hardening is continually extending: it may well be that special plant problems of these new fields may find their solutions in some of the highly ingenious devices which have been rejected or discarded by the industry for which they were originally designed.

3501. One of the early master patents in the oil-hardening industry¹ called for nothing more complicated than the bubbling of hydrogen through the heated oil in which the catalyst was suspended. Yet, as the art acquired more and more commercial importance, inventors came forward with proposals for apparatus of increasing complexity. The reasons for this are not far to seek: they fall into three groups. Chemists remembered the long struggle to produce saturated from unsaturated fatty acids on an industrial scale; they were impressed, perhaps obsessed, by the authority of Sabatier who had laid down² that contact between the liquid and the catalyst meant the arrest of the hydrogenation: some of them knew that certain chemists, expert in oil technology, if less so in catalytic technique, had declared themselves unable to obtain satisfactory hydrogenation by the simple means described in Normann's patent.³ It seemed incredible that the goal of this long and arduous quest should be attained by so direct and easy a path as the mere bubbling of hydrogen at atmospheric pressure through a mixture of hot oil and nickel. This was one cause of the deluge of patents for devices to produce contact, in specially favorable conditions, between the oil, the hydrogen and the catalyst. As a second cause, it is not uncharitable to suggest the desire to produce the same result with sufficient variation in method to allow of patent differentiation; colloquially, to sidestep earlier patents.

3502. A third kind of apparatus patent deals with real difficulties of the process, with such problems, for example, as the circulation of the hydrogen and of

¹ Normann, Eng. Pat. 1515, 1903.

² Para. 3506, footnote.

³ See para. 3511.

the oil, facilities for handling the catalyst, heat control and exchange, conversion of batch to continuous processes. Almost all the survivors belong to this third group.

3503. If it were necessary to classify apparatus for the industrial hydrogenation of oils there would be several characteristics which might serve as the primary bases. But, whichever we chose, we could not avoid overlap. Therefore, since a categoric classification is out of the question, we must content ourselves with a practical approximation.

3504. One of the chief differences depends on the condition in which the catalyst is maintained during operation. The catalyst may be free, i.e., suspended in the oil. Sometimes it is attached to a support, stationary or mobile, but not free. The first method, with the catalyst suspended in the oil, is much the most usual. This way of working is occasionally referred to by the not very happy name of the "powder process." The injunction to "keep your powder dry" prevents us from forgetting that powder may be wet: nevertheless, we habitually use the word "powder" with a connotation of dryness, probably because it originally meant "dust." A better term would be "suspension process," which would properly cover the case where the catalyst was on a fibrous carrier, such as asbestos, which could scarcely be called powder. A division of apparatus into those using catalyst in suspension and those in which the catalyst is fixed in place is nearly, but not quite coincident with another division—into batch and continuous processes.

3505. The essential intimate and frequently renewed contact between the oil, the hydrogen and the catalyst may be produced and maintained by the following means, which are arranged, more or less, in order of increasing complexity: 1. by the action of a stream of hydrogen, the hydrogen only being circulated; 2. by circulation of oil, holding catalyst in suspension, the mixture being presented to the gas as a spray or in some other tenuous form, e.g., a film; 3. by circulation of both hydrogen and oil, jointly or separately; 4. by agitation in a closed or in an open system, or by various combinations of the above.

HYDROGENATION OF FATTY ACIDS

3506. Of historical interest are the patents of Bedford ⁴ and of Schwoerer ⁵ since both show the influence of Sabatier's teaching to the effect that contact of liquid with the catalyst puts the latter out of action.⁶ Necessarily, therefore, these early patents dealt with fatty acids, which can be vaporized, and not with their glycerides.

⁴ U. S. Pat. 949,954, Feb. 22, 1910.

⁵ Schwoerer, U. S. Pat. 902,177, Oct. 27, 1908. Apparatus and method for hydrogenating fatty acids. The acids are atomized by superheated steam and hydrogen and exposed to the action of a catalyst in a special "helical pan."

⁶ Sabatier and Senderens, *Annales de Chimie et de Physique* [8], 4, 335 (1905), state that "Le métal ne soit jamais mouillé par un afflux excessif du liquide que l'on traite, ou à la suite d'un abaissement accidentel de la température du tube." They further say that in the preparation of cyclohexanol and its homologs from phenol or cresol at a temperature but slightly above the boiling-points of the latter bodies, sometimes by their condensation, the nickel becomes moistened and immediately becomes almost inactive, due, no doubt, to the surface becoming permanently changed in character by contact with the liquid phenol or cresol.

3507. In Bedford's apparatus a still or tower carries two beds of catalyst. This is said to be preferably nickelized pumice. By means of hydrogen under pressure, oleic acid is sprayed onto the lower catalyst bed. Hydrogen is admitted. A temperature of about 200° C. and a diminished pressure of about 50 to 100 mm. is maintained. The vapors of oleic acid mingled with hydrogen pass through the second catalyst bed, where more or less conversion occurs, then pass to the condenser, and finally collect in a receptacle. There is a connection to a vacuum pump.

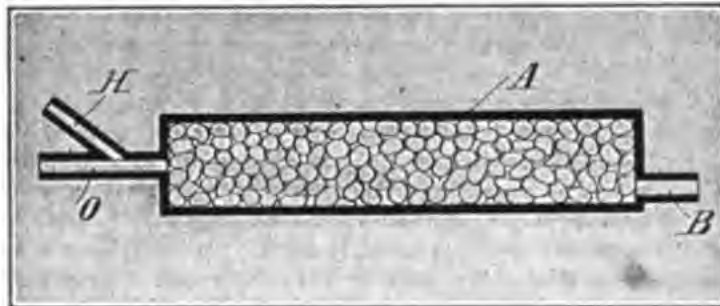


FIG. 43.

3508. The apparatus and method described in Brutzkus' British Pat. 155,776 of Dec. 22, 1920, are of a type which this inventor has applied more recently for the hydrogenation of petroleum. The analogy with the action in the Diesel engine is striking. Temperature and pressure are controlled by alternate compression and expansion. Fatty acid is sprayed into the compression chamber by a jet of hydrogen and the mixture there subjected to further compression.

3509. Normann states that he may carry out the hydrogenation of oils by treatment either in the form of vapors or as liquids. In the former case the fatty acid vapors together with hydrogen may be caused to pass over catalytic material carried by a pumice stone support. This may be represented by Fig. 43 in which

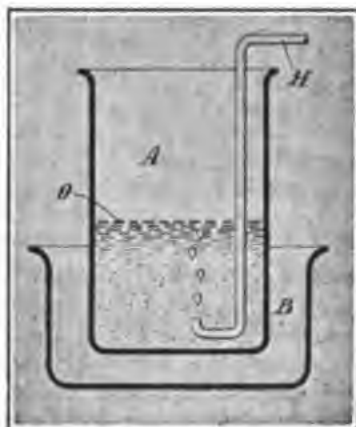


FIG. 43a.

A is a bed containing granular pumice coated with a metal catalyzer. *O* is an inlet for oil vapors and *H* is an inlet for hydrogen. The mixture passes through the tube *A* and the converted material is withdrawn at *B*. Normann quotes, however, that it is sufficient to expose the fat or fatty acid in a liquid condition to the action of hydrogen and the catalytic substance. He states that, for instance, if fine nickel powder obtained by the reduction of nickel oxide in a current of hydrogen is added to oleic acid, the latter heated over an oil bath and a strong current of hydrogen caused to pass through it for a considerable time, the oleic acid may be completely converted into stearic acid.

3510. Figure 43a shows very simple apparatus, such as might have been used by Normann to this end. *A* is a vessel containing oil *O* in which fine particles of

nickel are suspended while a strong current of hydrogen from the pipe *H* affords the hydrogen requisite for reduction of the oil. By this means Normann treated the fatty acid of tallow, having an iodine number of 35 and melting at about 46, thereby converting it into a body of improved color having an iodine number of about 10 and a melting-point of about 58. Normann also states that commercial gas mixtures, such as water-gas, may be used in lieu of pure hydrogen. The disclosures of the Normann patent are, however, rather meager and can hardly be considered to traverse comprehensively the difficulties encountered in the practical hydrogenation of oils in a liquid state.

HYDROGENATION OF OILS

CIRCULATION OF HYDROGEN

3511. As already mentioned, the first disclosure of the catalytic hydrogenation of oils in a liquid state is contained in the German patent 141,029, Aug. 14, 1902, to Leprince and Siveke, which corresponds to the British patent 1515, Jan. 21, 1903, to Normann. No agitation other than that produced by the current of gas is provided. This method, now used on a colossal scale, has proved surprisingly efficient. In 1913 Normann's English patent was declared invalid on the ground of insufficient disclosure (as to preparation of an active catalyst).⁷ According to *Seifen Ztg.*, 1914, 1260, the defect, which this journal oddly describes as "formal," was remedied and the amended patent reinstated. The patent having lapsed, the matter is no longer of importance.

3512. Ellis describes a process of the type which we are considering, but its main object is removal of "hydrogenation flavor" from the product. The pump *P* (Fig. 44a) circulates hydrogen through the mixture of oil and catalyst contained in the autoclave *A*. The hydrogenated product is run into the deodorizer *D*, where it is treated with superheated steam under diminished atmospheric pressure until the oil is freed from noxious gases or vapors. While the deodorization of ordinary cottonseed oil, for example, requires a temperature from 200° to 300° C. and a vacuum of down to 1 or 2 inches mercury, the deodorization of the hydrogenated cottonseed oil does not necessarily require as high a temperature and the vacuum "pulled" may be considerably less.⁸

3513. Another apparatus described by Ellis⁹ uses the hydrogen current to maintain the mixture. This process in one modification is concerned with the separation and retention of the catalyst at the end of a batch. The tank *A*,

⁷ Joseph Crosfield and Sons, Ltd. v. Techno-Chemical Laboratories, Ltd.; *The Illustr. Off. Journ. (Pats.)*, **30**, Rep. Pat. Des. and Trade Mark Cases, No. 12; 2nd edition, this work, Appendix A, 605-629. In this case the prior art was treated by the court as the art of oil technology and the expert witnesses relied on for the insufficiency of disclosure were oil experts, Hehner and Lewkowitsch. Had the plaintiffs impressed on the court the view that the prior art involved was catalysis (there being no prior art of oil hydrogenation) the result might, conceivably, have been different. Experts in catalysis knew how to prepare active nickel catalysts: it was (*semble*) irrelevant that oil technologists did not possess this knowledge.

⁸ U. S. Pat. 1,043,912, 1912.

⁹ U. S. Pat. 1,059,720, Apr. 22, 1913.

Fig. 44, contains a body oil *O*, the space above the oil being filled with hydrogen under any suitable pressure. The tank is heated by the jacket *S*. A pump *P* withdraws the hydrogen from the upper part of the tank and impels it through the pipe *D* into the lower part of the tank. The catalyzer is added to the oil when the proper temperature is reached and the constant bubbling of a stream of hydrogen through the oil causes intimate contact between the reacting elements. After the operation is completed, a porous plate, fastened to a movable stem in the upper part of the tank, may be depressed to fit into the bottom of the conical base so that when the oil is withdrawn a good portion of the catalyzer remains without exposure to the air and may be used with perhaps a small addition of fresh catalyzer for the treatment of a succeeding charge of oil. Rough filtration in this manner is an optional procedure.

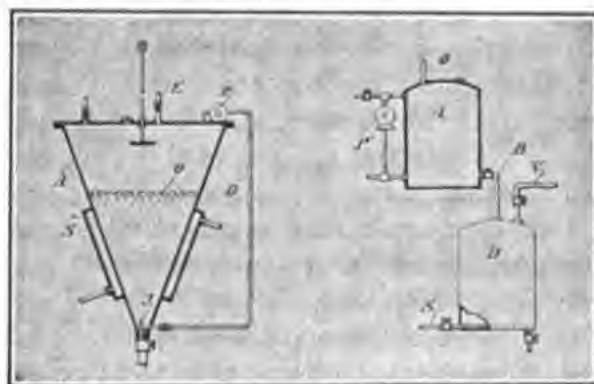


FIG. 44.

FIG. 44a.

3514. In a hydrogenation system involving the bubbling of hydrogen gas through a body of oil carrying catalytic material in suspension, the hydrogen may be transferred from one gas-holder to another, passing through the oil, while undergoing such transference, according to Ellis.¹⁰ In order to secure a better utilization of the hydrogen, it may be preheated by passing through a heat interchanger through which hot hydrogen issuing from the converter is conveyed.

3515. Agitation by circulation of hydrogen is also effected in an apparatus described by Ellis.¹¹ A tank of an elongated form is disposed with its long axis horizontal. Hydrogen is admitted by perforated pipes near the lowest part. Heating coils are so arranged below the level of the oil in relation to these hydrogen inlets as to permit and promote circulation of the oil with suspended catalyst. This circulation and the due admixture of oil and catalyst are maintained by the current of hydrogen. Baffles longitudinally disposed may be used. Provision is made for purification of the hydrogen and for heat interchange. The tanks may be of any suitable section—circular, D-shaped, V-shaped and so on. This apparatus is illustrated in Fig. 45.

3516. Adam¹² secures intimate contact between the reacting materials by

¹⁰ U. S. Pat. 1,247,095, Nov. 20, 1917.

¹¹ U. S. Pat. 1,480,251, Jan. 8, 1924, to Ellis, which is, in part, a continuation of matter contained in U. S. Pat. 1,294,068.

¹² *J.S.C.I.*, 1914, 1226; Brit. Pat. 24,815, Oct. 31, 1913.

bubbling the gas from a number of points into the body of liquid, coalescence of gas bubbles from adjacent delivery points being prevented by suitable partitions.

A form of Adam's apparatus is shown in Fig. 46.

In this apparatus a tall vessel *a* is provided with an assemblage of tubes *b*, supported by the supports *c*. These tubes are set closely together and are open at both ends. They may be of any desired cross-sectional form, and although shown straight may be somewhat spiralled where increased contact is desired. Beneath the tubes and at a little distance away is a gas manifold *d* connected to the gas supply duct *e* leading from the upper part of the vessel *f*, to the blower *h*. From the gas manifold nozzles *k* project into the tubes *b*. Gas is introduced at *g*.

By appropriate choice of the relative diameter and height of the tubes, the number of nozzles to each tube, and adjustment of the gas flow, and of the height of the liquid supplied

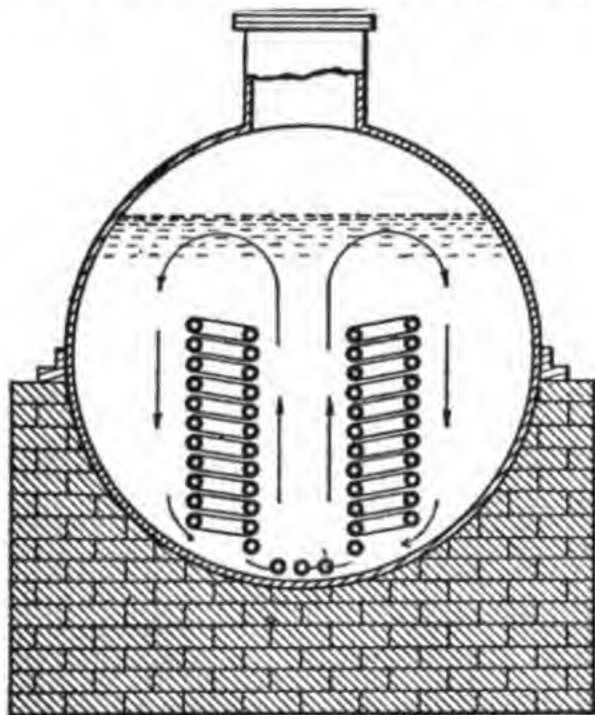


FIG. 45.

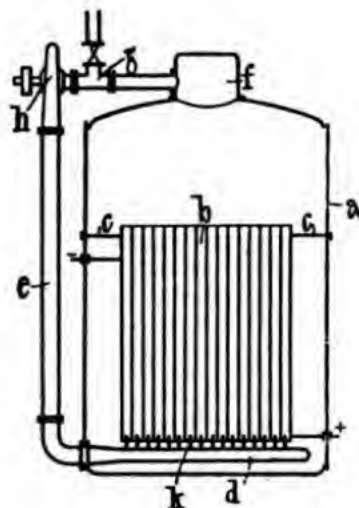


FIG. 46.

to the tubes the character of the contact can be varied from that of a climbing film to that of a tall column of froth.

The heating of the material can conveniently be effected by electric heaters immersed therein, and these may be formed, for instance, by insulating the tubes from each other at the top and bottom, and so converting them into a series of heating elements. See page 410.

3517. In order to produce agitation by means of the hydrogen current and to subdivide the latter, Holden ¹³ passes the gas through a porous diaphragm near the bottom of the reaction vessel. The gas is admitted under sufficient pressure to keep the oil and catalyst mixture above the level of the porous plate. The plate may be made of filtrox.

¹³ U. S. Pat. 1,485,926, Mar. 4, 1924 (assigned to Am. Cotton Oil Co.).

3518. A remarkable apparatus and method for hydrogenating oils (with a fixed catalyst) which has been used on the large scale, is described by Moore.¹⁴ The oil is fed in a continuous stream into the upper portion of a closed chamber, where it meets a blast of hydrogen and is atomized. The chamber is provided with a pervious filtering diaphragm containing a catalyzer, and the mixture of oil and hydrogen in excess penetrates the diaphragm into contact with the catalyzer whereupon the oil is saturated, and the hydrogenated oil and the excess of hydrogen pass into the lower portion of the chamber.

3519. The excess hydrogen may then be freed of oil and re-used, and the hydrogenated product withdrawn in a continuous stream. To secure the greatest possible active surface, the catalyzer consists of a layer of finely divided or pulverulent material confined between layers of filtering material. It is stated to be difficult to force a large body of oil through such powdery mass, but, when the oil is atomized, it may be forced through without difficulty if the pressure be sufficient.

3520. Moore finds that proper results cannot be obtained after the particles of the catalyzer become covered with films of oil, for the reason that the hydrogen is unable to obtain access thereto, and hence he provides for cleaning the catalyzer of the oil and thereby revivifying the former. This is accomplished by causing the constant passage of hydrogen through the catalyzer, and also by arranging the nozzles for the oil and hydrogen in such manner and so moving them that the spray is directed progressively toward restricted areas of the mass of catalyzer. Hence, in that portion of the catalyzer which at the moment is not receiving the spray, hydrogen is passing through in such quantities and at such velocity as to blow off or remove the films or coatings of oil which enclose the particles. Thus each restricted portion of the catalyzer first receives the mixture of oil and hydrogen, and is then freed of the oil, either as such or in saturated or partially saturated condition. By this procedure the quantity of oil which any one portion of the diaphragm and the catalyzer is receiving is relatively small, and the oil is so broken up and mixed with the hydrogen that it is readily carried through the catalyzer bed, and hydrogenated instantaneously, so it is claimed. By regulating the oil supply, the degree of solidity of the hydrogenated product is adjusted to any predetermined point, according to the use for which it is intended.

3521. In Fig. 47, an apparatus is shown consisting of a cast-metal casing forming a cylindrical chamber, transversely divided by a filter diaphragm containing the catalyzer. The diaphragm consists of a perforated plate, upon which rests a layer of wire cloth, preferably about 100 mesh. Upon the wire cloth is a thin layer of suitable inert material, such as a mat of asbestos fiber. Upon the layer of asbestos is a thin layer of the catalyzer, and upon this is placed another layer of asbestos. The oil and hydrogen are introduced into the upper compartment through down-turned nozzles. These nozzles are so located that the blast of hydrogen, traveling at high velocity, impinges upon the stream of oil flowing from the nozzle and atomizes the latter, directing the spray across the surface of the diaphragm. The nozzles revolve and thus direct the spray progressively in a circle over the entire surface of the diaphragm.

3522. The Moore process of hydrogenation used at the plant of the Berlin Mills Company, Berlin, N. H., is discussed by Hendricks, who states that a plant was established of a very highly developed semi-commercial nature with a capacity of 30,000 pounds daily.¹⁵

3523. Moore's process and apparatus may be compared with that of Bock,¹⁶ who describes several forms for the hydrogenation of oil and of fatty acids. One of these involves passing the fatty material along or through a porous plate con-

¹⁴ U. S. Pats. 1,121,860, Dec. 22, 1914; 1,184,480, May 23, 1916; *J.S.C.I.*, 1915, 144. Can. Pat. 172,839, Oct. 31, 1916.

¹⁵ *J. Ind. Eng. Chem.*, 9, 795.

¹⁶ *Chem. Abstr.*, 1915, 868; Dan. Pat. 18,332, Mar. 27, 1913; *Seifen. Ztg.*, 1914, 349; see also *Seifen. Ztg.*, 1914, 421.

taining catalyzer in the presence of hydrogen. Fatty acids may be hardened under a considerable degree of hydrogen pressure and subsequently the catalyzer may be freed from the acid by distillation under reduced atmospheric pressure. Reduced nickel on kieselguhr is used as a catalyzer. Either the hydrogen and fatty acids are allowed to pass in vapor form through the porous metal, or the oil is passed through the porous metal at the ordinary temperature and pressure while the hydrogen rises through the pores. These methods may be combined. The first method is preferred for fatty acids, the other for glycerides.

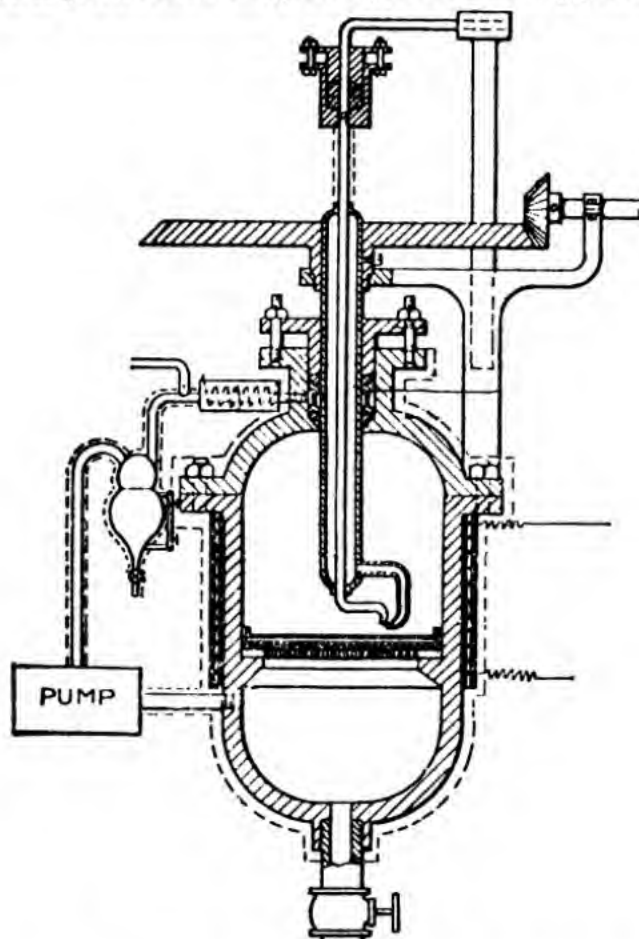


FIG. 47.

3524. An apparatus using the hydrogen pressure for circulation and agitation, and which is said to permit of either batch or continuous operation is described by MacDougall.¹⁷ In the axis of the main tank are disposed two concentric tubes with a narrow annular space between them. The tubes extend through the bottom of the tank, the inner tube is shorter than the outer tube and is open at the top and bottom. Thus, there is free communication between the top and bottom of the inner tube and the annular space. In the upper part of the outer tube is a series of "hit-and-miss" variable openings between the top of the annular space and the main tank. Below, the annular space communicates also with the main tank, but the openings here are so formed that there is suction from the main tank into the annular space. Heating (for starting up) is effected by an electric resistance element in the wall of

¹⁷ U. S. Pat. 1,381,319, June 14, 1921, assigned to Nat. Electro-Prod. Lt. and Brit. Pat. 150,802, June 5, 1919, to Withers; *J.S.C.I.*, 1920, 727A.

the part of the inner tube which projects below the main tank. The main tank and the tubes being filled with oil and suspended catalyst, hydrogen under 80 lb. pressure is admitted at the bottom of the inner tube. This, bubbling up the inner tube, forces up the oil-catalyst mixture which passes over into the annular space and so again to the bottom of the space and into the inner tube. The hit-and-miss (slide-damper) variable openings at the top of the outer wall of the annular space permit a regulated amount of the hydrogenated oil to flow on to the top of the raw oil in the main tank, a corresponding flow of raw oil into the annular space taking place through the suction holes below.

3525. By taking advantage of the difference in temperature between the hydrogenated and the raw oil, the former may be made to overlie the latter and the process rendered continuous: catalyst must, of course, be added to replace that withdrawn with the finished oil. For the somewhat complicated gas and oil connections the original must be consulted.

3526. The primary objects of the Radisson and Berthon¹⁸ apparatus, in which the hydrogen current produces the necessary agitation, are, first, the regulation of the temperature and of the quantity of catalyst to maintain an efficient rate of hydrogenation; second, to remove with the effluent hydrogen the excess of free fatty acid; third, to purify the hydrogen from these fatty acids and from water. The oil and catalyst mixture is contained in a jacketed "digester." The thoroughly desiccated hydrogen heated to the desired temperature is pumped into the bottom of the digester through a pipe at a pressure no more than sufficient to overcome the resistance in the circuit. The gas current is broken up by a perforated plate and is deflected by helically disposed plates on a paraboloid member and so passes through the body of the liquid. Through a nozzle a supply of additional catalyst mixed with oil is furnished, according to the progress of the reaction, from a jacketed apparatus. Hydrogen pressure is used for the injection. The temperature regulation is effected by flow of heated oil through the jacket of the digester. The issuing hydrogen undergoes purification as follows: It first passes through a heat exchanger where it heats up the incoming hydrogen. Part of the volatilized impurity is condensed here, but most of it in tubular water-cooled condensers, to which the hydrogen now passes, and in the next following washer which contains caustic soda. After passing through a water trap to arrest mechanically carried water, the washed gas enters a second heat exchanger where it is cooled by the gas issuing from the cooler. It now passes into a cooler (which need be only a quite small refrigerating engine of the carbon dioxide or sulphur dioxide type). Here it deposits all its water and issues dry, pure and ready for re-use.

3527. When used for alimentary oils this apparatus and process is stated to yield a product of such low acid value that the operation of neutralization may be omitted. In an example, 5000 kg. of soya-bean oil of 0.7 acidity gave a product of 0.2 acidity and 54° C. melting-point with three hours' treatment, during which the temperature was gradually raised to 300° C.¹⁹

3528. The most striking feature of the apparatus and method described by Boyce²⁰ is the operation under *reduced* hydrogen pressure. In other respects the method comes between those in which the hydrogen current effects all the agita-

¹⁸ U. S. Pat. 1,353,419, Sept. 21, 1920; Brit. Pat. 107,969, June 25, 1917.

¹⁹ Differential heating, according to progress of hydrogenation, is a feature of U. S. Pat. 1,026,156, May 14, 1912, to Ellis.

²⁰ U. S. Pat. 1,291,384, Jan. 14, 1919.

tion and those in which mechanical agitation is provided. A series of cylindrical reaction vessels or tanks is employed. Near the bottom of each is fixed a wire screen occupying the whole section. In the space *beneath* this screen are fan blades rotating on a vertical shaft. The hydrogen, under a plus pressure of 10 inches of water, is introduced into this space and, whirled by the fan blades, passes through the wire screen into the space above as a "mass" of fine bubbles in the oil-catalyst mixture. Above the oil column in the tank a vacuum of 5 or 6 inches of mercury is maintained. This causes an expansion of the gas bubbles and produces an intimate admixture of the reactants. A further advantage claimed is the reduction of the danger of explosion due to leakage of hydrogen. The tanks being operated in succession the hydrogen is completely used up, thus avoiding storage. The charge being introduced and drawn under reduced pressure, oxidation of the oil by contact of the air is avoided, and "the quality of the catalyst" is said to be preserved for the same reason. The greater part of the catalyst is allowed to settle out in the reaction tank.

3529. Nothing is said of the possible disadvantage of transferring the volatile and undesirable impurities from the contents of one tank to those of the others, by this system of series working.

3530. The purification of circulating hydrogen can be effected by causing the current of gas to pass into a larger volume of gas suitable for hydrogenation, and leaving at least the greater part of it in contact with water for a longer period than it was in contact with the organic material. By this means the gas is purified from acrolein and other undesirable volatile substances.²¹

3531. Although Normann's patent prescribed only a strong current of hydrogen to produce agitation many devices have been patented in which the hydrogen, under pressure, sprays or splashes the oil into a gas space.

3532. The minimum departure in this direction is effected by an apparatus described by McElroy²² and illustrated in Figs. 48 and 48a.

3533. A tank is provided with a steam-heating coil and hydrogen inlets and outlets. In the top, on the right-hand side, is an oil-charging pipe. On the top is situated a housing containing a pump or blower, the latter being arranged to draw in hydrogen from a point just below the top of the tank and to propel it to the bottom. The hydrogen discharges at that point through a revolving distributor shown in Fig. 48a. There is a pressure-equalizing opening in the housing floor. The tank is filled with oil to the level indicated. A screen is placed above the oil-level to serve to break up bubbles or foam. Nickel on pumice or coke is suspended in the oil and the contents of the tank are raised to 150° to 200° C. A pressure of hydrogen of 5 or 6 atmospheres is attained and the gas is caused to circulate from top to bottom by means of the blower in the housing. The discharge of hydrogen through the distributor causes the latter to rotate and sweep the bottom free of catalyst. Here, as in Normann's process, the reaction takes place in the body of the oil-catalyst mixture and the gas space serves merely to collect the hydrogen and to maintain the pressure. The essential characters of

²¹ U. S. Pat. 1,342,668, June 8, 1920, Ellis; *J.S.C.I.*, 1920, 551A.

²² U. S. Pat. 1,157,993, Oct. 26, 1915.

the McElroy apparatus are: 1, the rotating hydrogen distributor; 2, the screen to break up foam; 3, the fairly high pressure of hydrogen.

3534. Splashing into the gas space, the use of baffles and a series of reaction vessels characterize a process proposed by David.²³ The hydrogen, under pres-

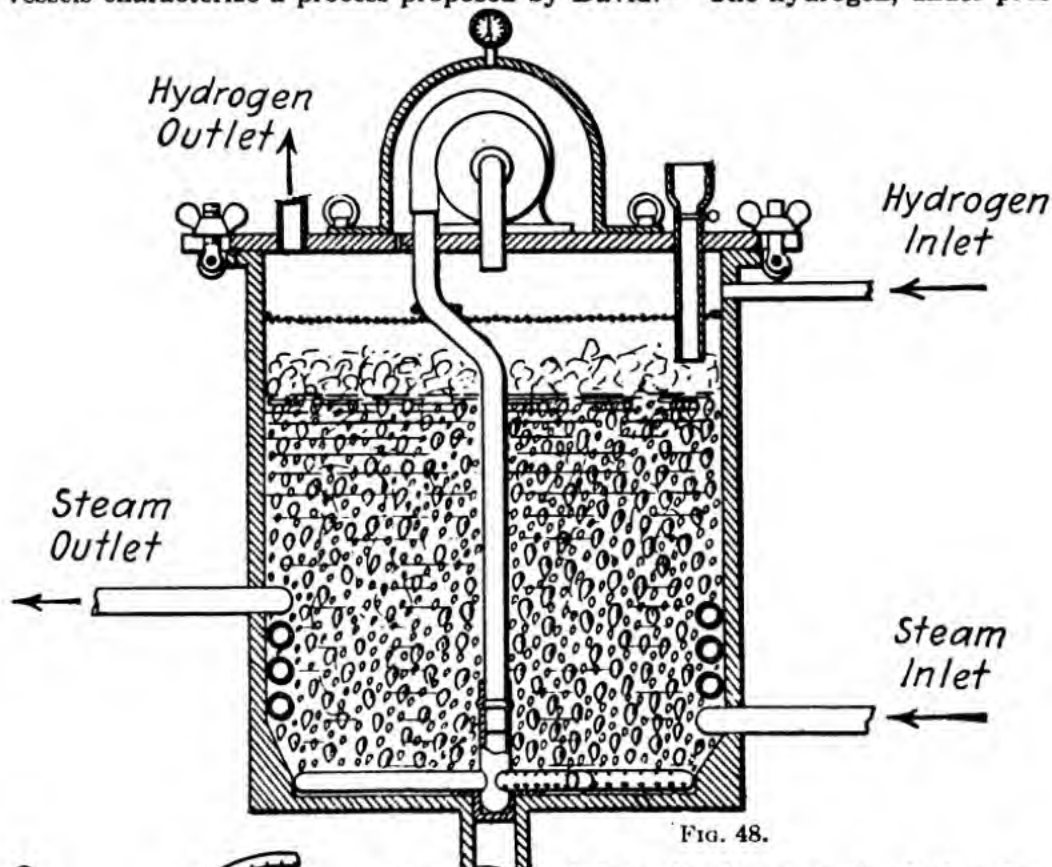


FIG. 48.

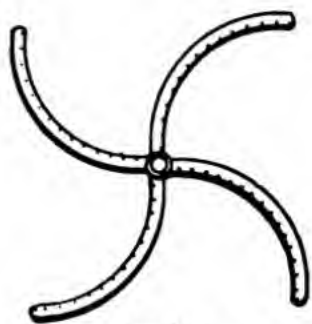


FIG. 48a.

sure, is forced into the lower part of the first of a series of connected cylinders containing the mixture of oil and catalytic agent. The oil is intermittently projected upwards and falls from depending plates, preferably of nickel, into the current of gas, while a hot-air jacket maintains the temperature at 150° to 200° C. The hydrogen passes through several of the cylinders before being returned to the gas holder to be purified, compressed, and used again.

3535. A device to overcome the difficulties of circulating hot hydrogen is described by Ellis.²⁴ The gas is circulated by means of an oil-sealed pump which may be so arranged as to permit the return of any hydrogen escaping through the stuffing boxes. Figure 49 shows this apparatus. 1 is an oil-treating tank with gas outlet 2, communicating with a drier or purifier 3. From the lower part of

²³ French Pat. 470,392, June 14, 1913; *J.C.S.I.*, 1915, 186.

²⁴ U. S. Pat. 1,071,221, Aug. 26, 1913.

the latter a pipe leads to the pump 4 which is enclosed by the housing 5, the space between pump and housing being filled with oil. The pump discharges into the lower part of the tank through the gas distributor 6. A connection 7 from the upper part of the housing to the tank provides a vent for gas escaping from the pump.

3536. A somewhat elaborate gas-measuring system has been proposed by deKadt.²⁵ The amount of gas absorbed by a liquid or other material in a closed vessel, for example, in the combination of hydrogen with fats or oils in the presence of a catalyst, is determined by means of a gas meter or other measuring instrument arranged on the pipe supplying the gas and adapted to cut off the supply when a certain amount of gas has been supplied or combined. When apparatus is used in which the gas is introduced through a fine-spray nozzle at the bottom of the liquid, and unabsorbed gas from the top of the vessel is withdrawn and again introduced into the liquid, two meters are fitted upon the inlet and outlet pipes respectively so as to act differentially upon an indicator needle which thus records the difference between the volume of gas supplied and the volume unabsorbed. The needle may control an electric contact by which the gas supply is shut off and the circulating pump stopped as soon as the requisite amount of gas has been absorbed.

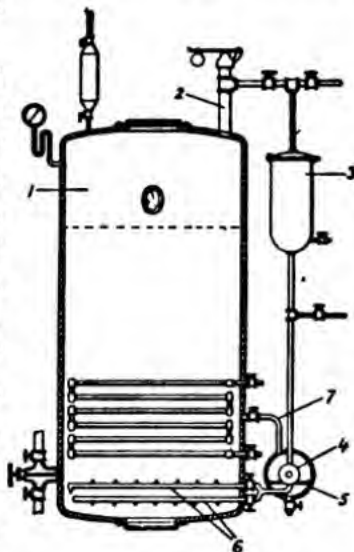


FIG. 49.

3537. Figure 50 shows the deKadt system.

The reaction vessel 1 is connected at its upper part through a suitable pipe connection 2 with a suction and force pump 3. At one part of its length this pipe connection 2 is formed into a cooling coil 4, which is located in a water reservoir 5. At the lower part of the reaction vessel 1 a nozzle or rose head 6 is provided, and from this nozzle a pipe 7 leads to the vessel 8 containing the hydrogen. This hydrogen-containing vessel communicates with the pump 3 by means of a pipe 9 and contains a cooling coil 12 provided with inlets and outlets for the supply and discharge of the cooling water.

The material to be treated, such as fats or oils, and the catalytically acting substances are supplied to the reaction vessel through a charging door 14. In the first place the hydrogen supply pipe 7 is cut off from the reaction vessel 1 and the pipe 9, connecting the hydrogen-containing vessel with the pump, is closed by a cock 15. The materials contained in the reaction vessel are then heated by means of a steam jacket or steam coil, and the air, contained in this vessel, is exhausted by means of the pump 3 and escapes to the atmosphere by way of the cock 16, the cocks 18 and 17 being open for this purpose. Hydrogen is then supplied through a pipe connected with the pump 3 and is forced into the hydrogen-containing vessel 8 through the pipe 9, the cocks 17 and 15 being open. When the necessary tension has been attained, the cocks 15 and 17 in the hydrogen supply pipe are closed and the cock 24 at the upper part of the reaction vessel connecting the vessel and pipe 2 are opened. A valve 19 is arranged in the pipe connecting the hydrogen vessel with the lower part of the reaction vessel by opening said valve 19, behind which a reducing valve 20 is arranged; the hydrogen is conducted by the pipe 7 into the vessel 1, where it passes from the nozzle 6 through the material to be treated with which it combines to some extent, while the excess escapes upwards and is again forced into the hydrogen-containing vessel 8 by the pump 3, the cocks being suitably adjusted. The supply of hydrogen contained in the vessel, which is not supplied

²⁵ Brit. Pat. 5,773, Mar. 7, 1912.

mented by a fresh external supply during the chemical reaction, must gradually decrease in tension owing to the combination with the contents of the reaction vessel. This decrease in tension can be utilized empirically for determining the progress of the chemical reaction or for ascertaining its various stages or its completion. These indications would, however, only be approximate and deKadt therefore provides means to interrupt the supply of hydrogen to the reaction vessel automatically after the consumption of the necessary quantity of combined hydrogen.

3538. With this object a gas meter 21 is arranged on the pipe 7 supplying the hydrogen to the reaction vessel and indicates the quantity of hydrogen passing from the container 8 into the reaction vessel 1. A similar meter 22 is arranged on the return pipe 2 and measures the quantity of gas being withdrawn. Both these meters act on an indicating shaft in such a manner that by the rotation of the shaft the first gas meter 21 moves the hand of an indicating shaft upwards, while the other gas meter 22 moves it rearwards so that the index hand shows the difference, that is to say the consumption of hydrogen. An electric contact is

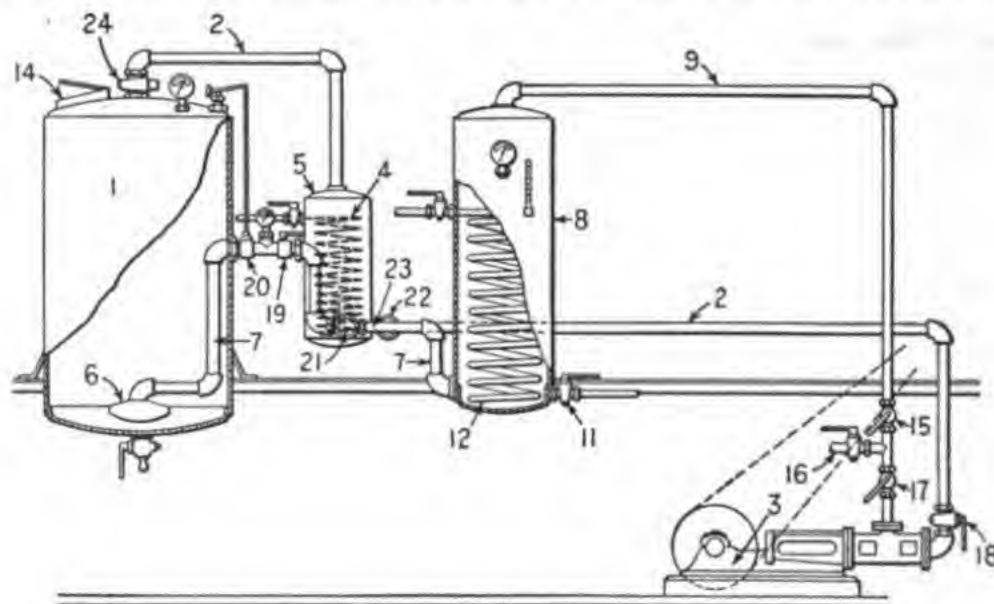


FIG. 50.

arranged in the path of the index hand and when it reaches a certain position, in which the necessary quantity of hydrogen has been consumed, the circuit is closed, and the hydrogen supply is cut off.

CIRCULATION OF OIL

3539. The oil circulation method finds its simplest expression in Hoehn's apparatus. Hoehn is opposed to agitation, even by the gas current. His method is to expose a large surface of the oil to hydrogen in fairly deep pans. Figure 51 shows, diagrammatically, the Hoehn apparatus. A tight housing encloses a series of pans in which the oil-catalyst mixture is exposed to the gas. The oil enters the lower pan and is pumped successively to the intermediate and upper pans, finally returning to the lower pan. The saturated oil may be drawn off from any one of the pans through outlets near the bottom (shown in the drawing midway of the pan).

3540. Contrary to the opinion entertained by many Hoehn holds it unnecessary to agitate violently the catalyzer for the purpose of contacting it with

hydrogen. Once the catalyzer is wetted with the oil there can no longer be any actual contact with the gas. Hydrogen reaches the catalyzer seemingly only through solution in the oil. The forces of adhesion effectually seal the catalyzer surface from the gas, and no measure of agitation by ordinary mixing apparatus will dislodge the film of oil. Of course, agitation secures the rapid replacement of more saturated by less saturated portions of the oil, but this replacement, under certain conditions, may proceed rapidly, simply by diffusion.

3541. The British patent to Bedford and Williams, 2520, of 1907, contains probably the first published description of a method of exposing oil to the action of hydrogen by treating the oil in films in an atmosphere of hydrogen and in contact with a catalyzer of the nickel type.

3542. The statement of invention is as follows:

A. "The invention consists in bringing the substance to be treated—in the liquid state or in solution—into contact with the catalytic substance in the form of fine drops or spray or as a film, and so that the catalytic substance and hydrogen are in excess.

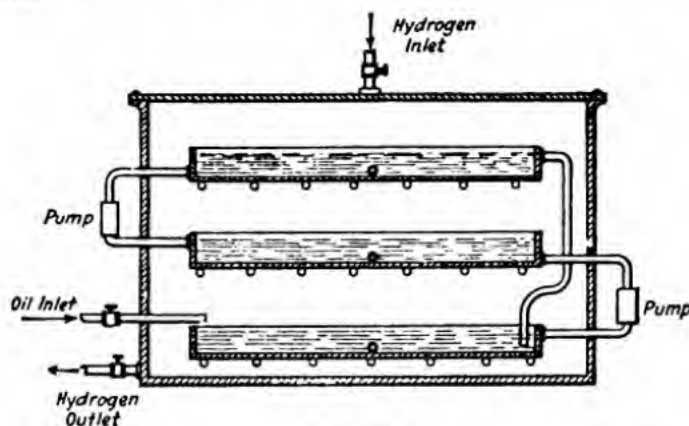


FIG. 51.

B. "The invention also consists in continuously passing the substance to be reduced—by itself or in solution—introduced in the form of spray or fine drops over the nickel or other catalytic substance with or against a current of hydrogen so that a continuous supply of reduced substance can be obtained.

C. "In carrying out the invention according to one mode when nickel, for example, is used as a catalytic substance, it is deposited on its support for the reduction from its nitrate, the substance which is to form the support for the nickel—say pumice stone, porous earthenware or the like—being placed in the nitrate solution which is allowed to stand for some time after which the excess of solution is drawn off, or the nitrate solution is allowed to flow on to the support in vacuum. The pumice stone or other support is then heated over a fire (in a crucible) to convert the nitrate into oxide. If the layer is too thin the operation of soaking in nitrate solution and heating must be repeated. Finally it is introduced into a suitable receptacle or tower and heated to say from 275° to 300° C. in a current of hydrogen with or without the addition of ether or other suitable

organic vapor to convert the nickel oxide into nickel and as soon as reduction is complete the contents are allowed to cool to the temperature at which the reduction is to take place (e.g., for oleic acid and oils 160° to 200° C.).

D. "As soon as the conversion of nickel oleate or nickel nitrate to metallic nickel is complete the contents are allowed to cool to the temperature at which the reduction of the organic substance is to take place. The substance to be reduced is fed into the top of the tower in the form of spray or the like and a current of hydrogen is forced in from below to mingle with the same, the mixture being thereby exposed to or brought into contact with the nickel, which causes the substance to be reduced. The substance leaves the tower in a reduced condition and free of nickel or nickel compounds, the reduced substance being drawn off as it is formed, preferably continuously. In order to obtain a spray the liquid may be fed into the tower through a screen or plate provided with a large number of small holes or capillary tubes.

E. "According to this manner of carrying out the invention the unsaturated liquid or other substance to be reduced flows in drops or as a spray or as a film over the nickel-coated material and is thus exposed simultaneously to large surfaces of nickel and hydrogen, both the latter being in excess.

F. "Though the description is of a spray method, it is not of the oil-catalyst spray type, as in Testrup's apparatus, because the catalyst is fixed. The spraying serves merely to insure a uniform flow of the oil through the catalyst bed."

3543. The Erdmann German patent 211,669 of Jan. 19, 1907, in the first described form differs from the Bedford and Williams procedure just described only in the interposition, between the spray and the catalyst bed, of a rotating cylinder coated with nickel catalyst. The second modification seems identical with the Bedford and Williams invention.

3544. In a supplement patent 221,890, 1909, Erdmann recommends the steam distillation from the reaction chamber of the saturated product, under diminished pressure.

3545. A development of this method is seen in an apparatus described by Verona Rinati²⁶ for the hydrogenation of oils, in which palladium precipitated on small pieces of coke is used as a catalyst.

The catalytic material is placed on a movable support kept in motion by a rotating spindle connected by gearing with a pulley outside the reaction chamber. Oil which has previously been heated is sprayed into the upper part of the chamber by means of hydrogen under pressure, and a pressure of about 2 atmospheres is maintained inside the chamber. Three reaction chambers are provided and the oil may be withdrawn after one, two, or three treatments, according to the degree of hydrogenation desired. The hydrogen is obtained from water-gas by the Frank-Linde-Caro process of refrigeration, and all the excess coming from the reaction chambers is returned to the refrigerating apparatus for purification. When the catalyst loses its activity, it is washed in the apparatus with an inert solvent (benzine), the last traces of the latter are expelled by a current of steam, and the palladium is again rendered active by treatment with hydrogen at not above 150° C. Palladium possesses the advantage of being active at a considerably lower temperature than nickel (e.g., at 80° to 90° C.).

3546. Among apparatus and methods in which the oil is circulated we find several which employ the device of spraying the oil-catalyst mixture into the gas space.

²⁶ *Annali Chim. Appl.*, 1914, **2**, 99-105; *J.S.C.I.*, 1914, 1061; *Chem. Abst.*, 1914, 3723.

3547. In the trial of the case, already mentioned, where the validity of the Normann patent was in issue it was shown that the defendants (Techno-Chemical Laboratories, Ltd.) had used (perhaps to set up a test case) a pilot plant. This consisted of a cylindrical autoclave 1 meter high and $\frac{3}{4}$ meter in diameter (inside measurements,) with a steam jacket, and fitted with a non-conducting lining of unknown material. Nine kilograms of cotton oil were pumped into the autoclave, and 288 g. of a composition, containing a catalytic agent, were used and were mixed with the oil prior to the introduction of the mixture into the autoclave. The autoclave was then filled with hydrogen from a cylinder to a pressure of 15 atmospheres. During the operation the pressure varied from time to time according to the absorption of hydrogen. A mechanically driven circulation pump was connected with the autoclave both by its suction and delivery conduits. By means of a pump and a jet for spraying, a mixture of oil and composition containing the catalytic agent was drawn from, and forced back into, the autoclave.²⁷

3548. With mechanical circulation of the oil-catalyst mixture agitation may be effected by suitably disposed baffle plates. An apparatus of this kind which is industrially important is that of Maxted.²⁸ This will be described in more detail when we come to consider complete plants for oil hydrogenation. The principal element is a tower provided with a number of fixed baffle plates shaped like propeller blades. These are superposed on one another and are alternately parts of left-handed and of right-handed screws. Through this column the oil-catalyst mixture is "projected" (which does not seem to mean anything other than "pumped") together with hydrogen. The action of the baffles is to cause rotation of the mixture alternately clockwise and anti-clockwise.

3549. The apparatus of Schlostein²⁹ is intended to permit of hydrogenation and deodorization being performed in the same vessel. The oil circulates in a closed system. Perforated pipes force the deodorizer (e.g., steam) or the hardening agent (i.e., hydrogen) through the oil.

3550. A frequently used device is that of causing the oil to flow over baffles of some kind so as to expose it in a thin film to the action of hydrogen. Thus Humphreys hydrogenates oil with an apparatus consisting of a closed chamber (Fig. 52) having within it slightly inclined, supporting plates, one above the other, and successively discharging at their lower edges onto the upper portions of the next succeeding plate with means at the bottom of the chamber for collecting the material being acted upon and delivering to a pump which conveys it back to the top of the chamber to complete the path of circulation.

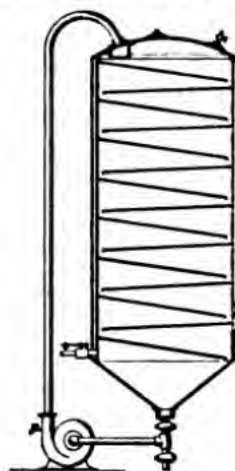


FIG. 52.

²⁷ *Brit. Off. Jour. Suppl.*, June 18, 1913, 301. This seems to be the apparatus and method described in Swed. Pat. 992, May 27, 1911, to Techno-Chemical Laboratories, Ltd.

²⁸ *Brit. Pat.* 109,993, 1916, to Maxted and Ridsdale; *U. S. Pat.* 1,313,407, Aug. 19, 1919.

²⁹ *U. S. Pat.* 1,296,013; *Chem. Abst.*, 1919, 1539.

3551. In the same order of ideas is Sojiro Kawase's apparatus.^{29a} This consists of a tower in the center of which is a vertical rod. To this rod are attached perforated plates at a slope of 60°. Down the "stairs" so formed the oil-catalyst mixture cascades, meeting the up-coming hydrogen current.

3552. The Société Anonyme l'oxyhydrique française has proposed a detail in the technique of hydrogenation which consists in passing the hydrogenated oil, holding catalyst in suspension, through an asbestos filter. This retains the catalyst. The new batch of oil coming through the filter in the reverse direction takes up the catalyst.³⁰

DOUBLE CIRCULATION—HYDROGEN AND OIL

(WITHOUT MECHANICAL AGITATION)

3553. A rather complicated oil-catalyst mixture circulation apparatus is described by Martin.³¹ A reservoir contains the oil-catalyst mixture. It has a gas space above. Into this the oil is pumped from the circuit or from the supply of raw oil or from both. The mixture passes by gravity, through a valve in the bottom of the reservoir, into conduits. These conduits are jacketed for heating and heat-regulation. In these conduits are perforated pipes connected with a hydrogen pump. This, drawing gas from the gas space and from the general supply, forces it through the perforations into the circulating oil-catalyst mixture. The residual gas accompanies the oil to the reservoir, thus completing the circuit.

3554. Two somewhat related methods of hydrogenation by spraying the oil-catalyst mixture into hydrogen under pressure are described in patents to Testrup³² and to Wilbuschewitsch.

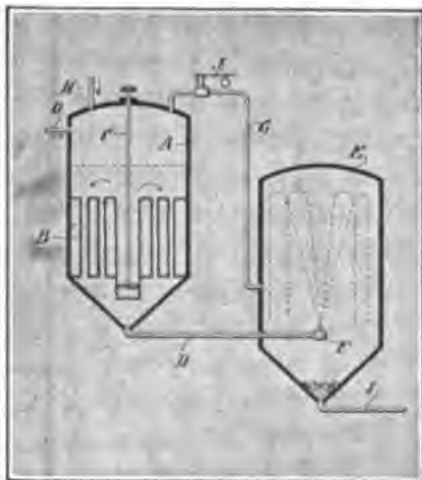


FIG. 53.

3555. Testrup's process and apparatus is described in Brit. Pat. 7726, of 1910, and is illustrated in Fig. 53. Oil and catalyzer are pumped through the pipe *O* into the tank *A*, and hydrogen is admitted by the pipe *H* to furnish a gas pressure of, say, 15 atmospheres. The tubes *B* are heated by steam and the stirrer *C* circulates the oil and catalyzer in the tank *A*, until the oil has become heated and presumably somewhat hydrogenated. The oil is allowed to pass into the adjacent tank *E*, entering this tank by the spray nozzle *F*. Hydrogen gas is admitted

to the tank *E* from the tank *A*, so as to afford a pressure of, say, 12 atmospheres in the tank *E*. A series of tanks may be arranged with a constantly decreasing

^{29a} Japanese Patent 37,301, Oct. 19, 1920; *Chem. Abst.*, 1922, 170.

³⁰ Brit. Pat. 143,848, May 11, 1920; *Chem. Abst.*, 1920, 2296; reference to Brit. Pat. 127,978.

³¹ U. S. Pat. 1,333,328, Mar. 9, 1920; Brit. Pat. 129,461.

³² Testrup was co-defendant with Techno-Chemical Laboratories, Ltd., in the case of the Normann patent and counsel stated that this spraying process was Testrup's invention.

pressure so that the differential pressure enables the spraying of the oil from tank to tank. Testrup states that spraying the material ten or fifteen times is sufficient to bring an oil of an iodine number of 110 down to an iodine number of 50.

3556. According to one form employing the apparatus shown in Fig. 54, and treating cottonseed oil, the oil, mixed with a suitable contact substance, such as finely divided palladium or preferably nickel, is placed in a vessel *a* provided with a stirring device *b* comprising blades or like elements fixed to a vertical and rotatable shaft *c* within it. The amount of nickel may be about 2 to 3 per cent by weight. This vessel is preferably jacketed as at *d*, and is heated by the passage of heated fluid through this jacket, say to about 160° C. From this chamber the oil is pumped by a pump *f* through a conduit *f* and enters a vessel *g*, which is

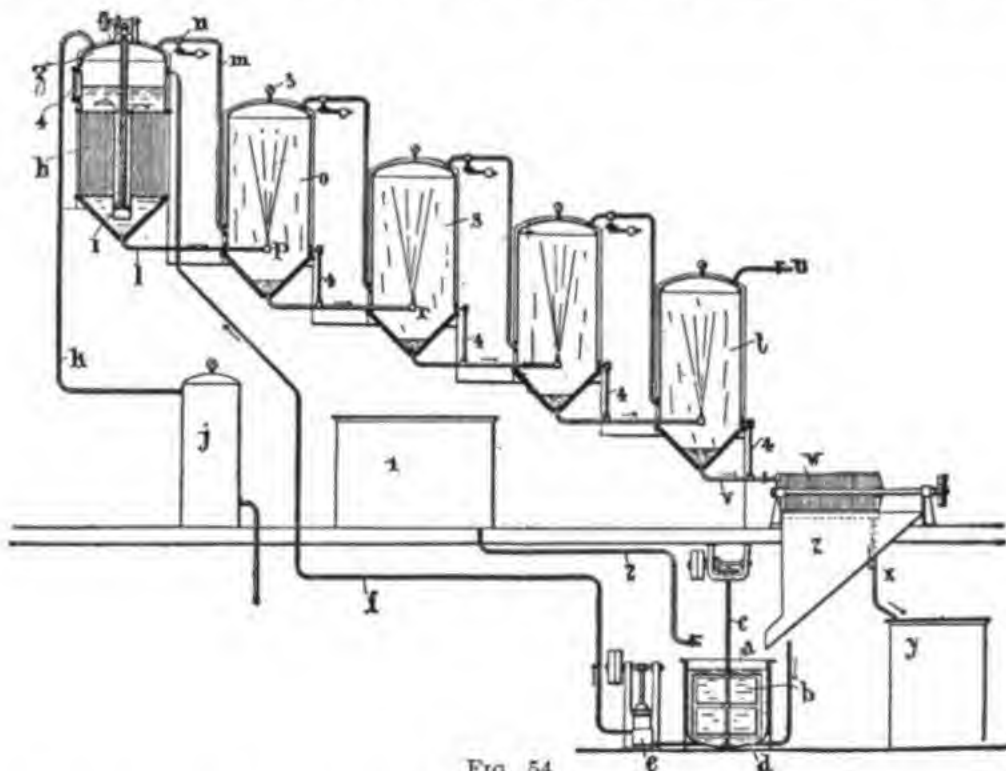


FIG. 54.

jacketed and heated by tubes *h*, being also provided with a mixing device comprising a central tube and propeller arrangement *i*. Hydrogen gas is supplied at high pressure from a reservoir *j* through a duct *k*. The vessel *g* has an educt *l* for the material under treatment at its base and an educt for hydrogen *m* provided with a loaded valve *n*. The duct *m* opens into a vessel *o* into which the oil from the vessel *g* is sprayed by a spray nozzle *p* attached to the end of the duct *l* by the pressure of the gas in the vessel *g*. The oil and catalyst thus exposed to the action of the gas fall into the base of the vessel *o* to be forced by the pressure of the gas therein through a duct to a nozzle *r* in another vessel *s* wherein the operation is repeated. Several such vessels are arranged in this way in cascade, all being jacketed to allow of maintaining the desired temperature. The last vessel *t* is provided with any suitable educt *u* for the gas and an educt *v* for the treated oil and catalyst which is passed to filter press *w* in which the oil is separated from the catalyst, the former passing by a duct *x* to a reservoir *y* and the catalyst being returned to the vessel *a* for which purpose the chute *z* may be utilized. Should the catalyst have become contaminated with nickel soap it may be purified as by washing with acid. A storage tank for the material awaiting treatment is indicated at *1* with its duct *2* leading to the vessel *a*. Gauges for noting the pressure *3* and the level gauges

4 are also employed. The temperature at which the reaction is conducted is about 160° to 170° C., and the pressure of the hydrogen in *g* may be about 15 atmospheres, in *o* say 12 atmospheres, the difference in pressure producing the spray. The pressure may similarly fall by 3 atmospheres for each vessel. It may be necessary to pass the substance again through the apparatus or to provide several systems of heaters and spraying devices in series in order to obtain the desired result but by this process the requisite number of repetitions can be carried out rapidly. Even such a number of treatments as stated above requires only about thirty minutes or less and the number of treatments would depend largely on the activity of the catalyst employed.

3557. The Wilbuschewitsch plant is a rather complicated system, and Fig. 55 shows only what appear to be the essential features of the treating apparatus.

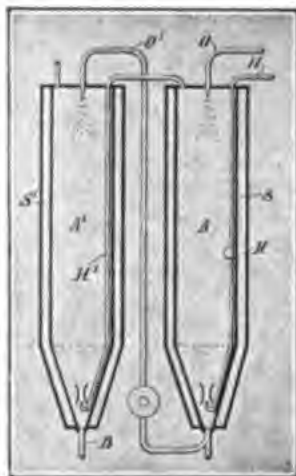


FIG. 55.

Several tanks or autoclaves are connected as shown at A and A', oil entering the top of the tank A by the pipe O, to form a spray which in descending meets an upward current of hydrogen entering by the pipe H. The oil is drawn off through the pipe O', and sprayed into the tank A'. This time it meets a current of hydrogen represented by the excess of hydrogen coming from the tank A. The treated oil is drawn off and may be centrifuged to remove the catalyzer. A pressure of 9 atmospheres is recommended and the pressures may be varied in the different tanks.³³

3558. Of the Wilbuschewitsch process Goldschmidt states that the high hydrogen pressures employed enable the reaction to take place quickly at temperatures between 100° and 160° C., so that

the fat is not likely to be injured by the temperature to which it is subjected.³⁴

3559. Another apparatus for hardening oil, proposed by Wilbuschewitsch,³⁵ comprises the vessel R (Fig. 56) containing the fat to be treated and the vessel O containing the catalyst. Differentially connected pumps AA' feed the oil and the catalyst into the mixing device B in which an intimate mixture of the oil and the catalyst is obtained. This mixture passes through a pipe G and the valve H into an autoclave J' which is provided with a spraying device C' consisting of a number of spraying nozzles so arranged that the oil and catalyst are uniformly scattered in finely subdivided condition throughout the whole inner space of the autoclave. A compressor K forces hydrogen into the autoclave under a pressure of about 9 atmospheres. The pipe X extends from the upper part of the autoclave downward to the lower end of the same and is provided at its lower end in the conical part of the autoclave with an admission nozzle D'. By this spraying system an intimate contact of the oil mixture with the hydrogen is achieved on the counter-current principle. The autoclave is heated to between 100° to 160° C. according to the nature of the oil under treatment. The reduction by the

³³ U. S. Pat. 1,024,758, Apr. 30, 1912.

³⁴ *Chem. Ztg.*, 1912, 945.

³⁵ U. S. Pat. 1,079,278, Nov. 18, 1913.

hydrogen begins at the upper part of the autoclave. The partially reduced oil mixture collects in the conical part of the autoclave and is sprayed in the form of a fountain through the autoclave by the incoming hydrogen. The mixture is forced by pump *E'* into the second autoclave *J*². The hydrogen enters this autoclave through pipe *Y* and the action of the first autoclave is repeated. Any number of such autoclaves can be arranged in series or parallel to each other in accordance with the extent of reduction required. It is generally suitable to use one autoclave for each increase of melting-point by 15° C. When the fat has attained the desired melting-point which is ascertained by samples withdrawn from the autoclaves, the oil mixture is withdrawn through the valve *U* into the centrifugal apparatus *F*. Here the oil is separated from the catalyst. The finished reduced oil flows into the reservoir *N* while the catalyst is returned through the pipe *R'* and valves *S* and *T* to the vessels *O* and *P*.

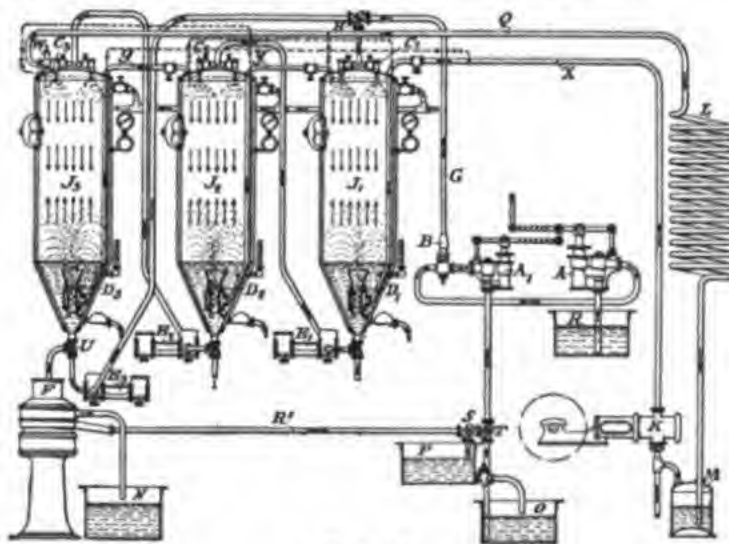


FIG. 56.

3560. At first when the catalyst which Wilbuschewitsch employs is still quite fresh, he states that 1 per cent may be used. When, however, in the course of the operation its catalytic power decreases, correspondingly more of it must be present. The regulation of the quantity of catalyst may be attained by a suitable adjustment of the differential pump system.

3561. When the catalyst is completely spent it is allowed to flow out through the valve *S* into the reservoir *P* in order to be regenerated. The working is continued by introduction of fresh catalyst through the valve *T*. The hydrogen not consumed passes through the check valve *W* and pipe *Q* and cooling worm *L* into a vessel *M* filled with caustic soda lye where it is purified and then passes to the compressor and autoclaves.

3562. Wilbuschewitsch regards his process as applicable to the treatment of all unsaturated acids and their glycerides, as well as for waxes and other alcoholic fatty substances. From castor oil there is obtained a product which melts

at 83° C. The finished fat can be hydrolyzed and the fatty acids distilled. For example, from cottonseed oil there may be obtained fatty acids which melt up to 71° C. and make excellent candles. After suitable refining the products may

yield satisfactory alimentary fats if the reduction is only carried so far that the melting-point is between 28° and 34° C. Thus he finds from castor oil there may be made a product which is odorless and tasteless, but retains the other properties of castor oil. So also from cod-liver oil and other fish oils there may be made butter substitutes, or from vegetable oils substitutes for cocoa butter. Oils treated by the process lose their specific odor.

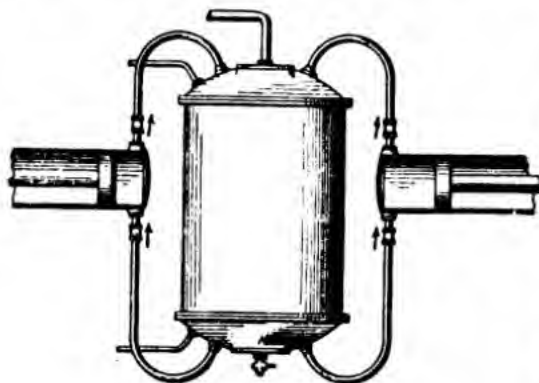


FIG. 57.

3563. Mandelstam hardens oil by a combined spraying and bubbling method employing apparatus as shown in Fig. 57. A closed tank heated by a steam coil is two-thirds filled with oil carrying a catalyzer in suspension. The pumps shown on either side of the tank withdraw the oil and catalyzer mixture from the lower part and spray it into the gas space in the upper part of the tank. Hydrogen is admitted by the pipe shown in the middle of the top of the apparatus and is forced into the oil at various places in the tank by means of sprayers or distributing devices.³⁶

3564. For the effective mixing of oil, catalyzer and hydrogen, Ittner³⁷ recommends an apparatus of the character shown in Fig. 58.

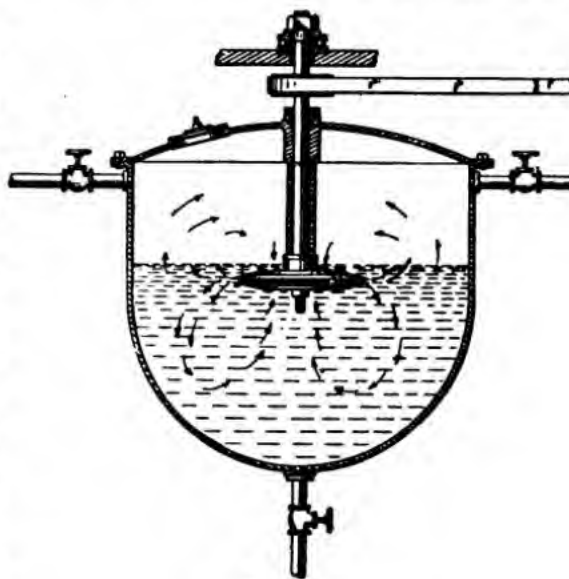


FIG. 58.

In this drawing a receptacle containing oil is equipped with a peculiar form of agitating and hydrogen-mixing device shown in detail in Fig. 58a. The latter is termed by Ittner a centrifugal distributor or injector. It is set below the normal level of the oil and is so constructed that the liquid is drawn in near its center and discharged centrifugally outward so that circulation of the liquid is effected. The upper part of the chamber is filled with hydrogen gas which may be at atmospheric pressure or under increased or decreased pressure.

³⁶ *J.S.C.I.*, 1914, 1162; U. S. Pat. 1,114,623, Oct. 20, 1914.

³⁷ U. S. Pat. 1,242,445, Oct. 9, 1917; *Cf.* 1,271,576, July 9, 1918, to same patentee.

The gas is drawn through the hollow shaft of the centrifugal distributor by means of perforations and passes out through the disc-shaped portion admixed with oil. By this means Ittner states, an intermixture of the liquid and gas of such intimacy is obtained that ordinary

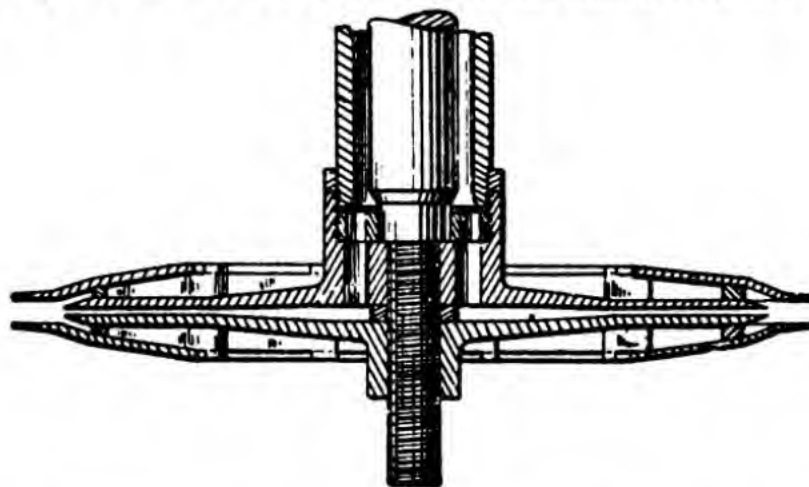


FIG. 58a.

agitation can add but little to the efficiency of the operation. In fact, he states it is sometimes advantageous to avoid a high degree of agitation of the liquid and screens or baffles may be so placed as to lessen agitation.

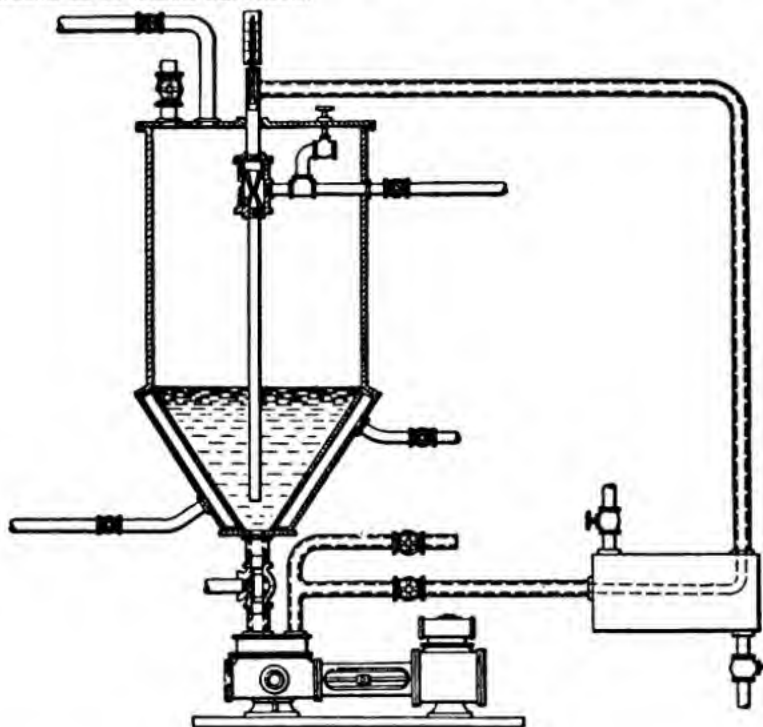


FIG. 59.

3565. Ittner ²² also effects this mixture of gas and oil in another manner shown by Fig. 59. The oil-catalyst mixture is pumped from the bottom of the

²² U. S. Pat. 1,271,575, July 9, 1918.

reaction vessel and reenters from above. The aspirator device communicates with the gas space. The gas is, therefore, entrained with the oil-catalyst mixture and carried into the body of the oil, with which and with the catalyst it forms an intimate mixture.

3566. Birkeland and Devik ²² employ a form of apparatus which permits of forcing a mixture of oil and catalytic agent downwards through a nozzle into an atmosphere of hydrogen, filling the space above the bulk of the oil, which is contained in an autoclave. The hydrogen is drawn into the oil jets by injector action and subsequently rises in small bubbles through the body of oil. The process is preferably carried out under a pressure of 10 to 15 atmospheres and at a temperature of about 150° C. Sudden reduction of the pressure is claimed to promote the hydrogenation of the oil. Details of the apparatus are shown in the accompanying illustration. Figure 60 is a hydrogenating apparatus shown in sec-

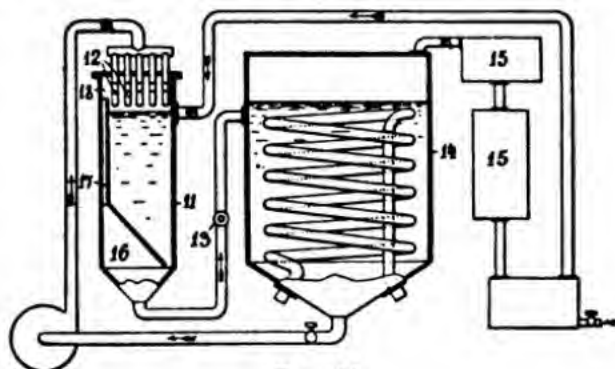


FIG. 60.

tion. Birkeland and Devik state that when an efficient catalyzer, for instance pyrophoric nickel, and a good oil are employed, the hardening will be effected in from one-half to one hour.

3567. They observe that it is advantageous to employ injectors which are so constructed that the shape or thickness of the oil jet may be altered, because such alterations during the working have proved to be necessary in order to obtain at each moment the best possible atomization and distribution of the gas in the liquid. To obtain this a member adjustable from the outside may be provided in the injector. The oil is introduced into the vessel 11 through adjustable injector nozzles 12, so as to produce a mixture of the very hot oil with hydrogen. This milky-white mixture, in which the bubbles of hydrogen are too small to be observed with the naked eye, is then introduced through a reduction valve, 13, into a larger vessel, 14. Birkeland and Devik claim to have found that under this expansion the intimate mixture of oil and hydrogen gives off malodorous volatile substances which may be condensed and washed out by passing the gas through a condensation and washing apparatus, 15. This is stated to have the advantage of eliminating several substances (volatile amines, water, etc.) before the addition of the catalyzer so that on the one hand an unnecessary inactivation of the catalyzer is obviated, while on the other hand hydrogen is consumed only for the purpose of hardening the oil itself and not for the hydrogenation of the volatile bodies. The hydrogen gas, after having passed through the vessel, 14, and having thereupon been purified, is then again compressed and brought into circulation anew by being introduced into the hydrogen space, 18. When the oil has in this manner been freed from various malodorous

²² U. S. Pat. 1,125,259, Jan. 19, 1915. See also 1,271,575 and 1,271,576 issued July 9, 1918, to Ittner.

volatile substances the hardening process may be started by adding the catalyzer to the oil. During the hardening operation the same circulation as before described may be maintained or the inlet to the expansion tank may be closed and the oil maintained in circulation only through the pressure vessel, 11.⁴⁰

3568. The direct pumping of hot hydrogen gas, especially if the latter is under considerable pressure, offers some difficulties, and the apparatus shown in Fig. 61 is designed to effect a circulation of the gas by inductive effect. The tank 1 carries an inductor 2 through which is forced oil propelled by the pump 3. The passage of the oil through the inductor causes hydrogen, which is supplied to the upper part of the tank, to be drawn into the central vertical pipe and carried with the oil to the bottom of the tank

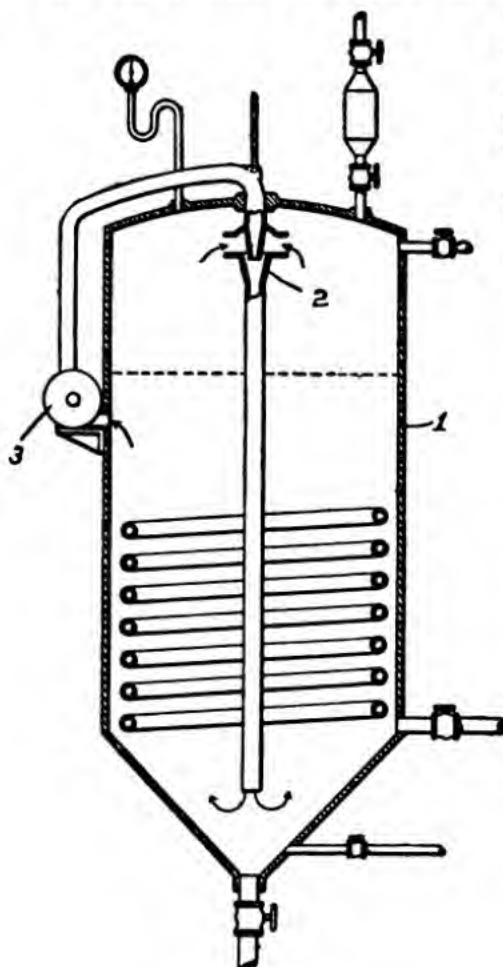


FIG. 61.

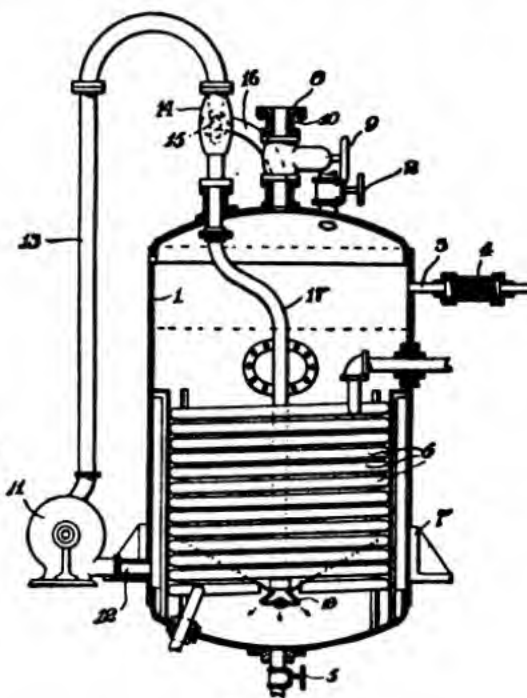


FIG. 62.

when the gas bubbles through the main body of oil. Thus the oil which is being treated is made use of to circulate the gas.⁴¹

3569. A modified form of the inductor and tank shown in Fig. 61 is depicted in Fig. 62.⁴²

In Fig. 62, 1 is a treating receptacle having the inlet 2 for oil or catalyzer; a hydrogen inlet 3; a back-flash tube 4; a draw-off valve 5; a steam-heating coil 6; supporting members

⁴⁰ French Pat. 456,632, Apr. 14, 1913; U. S. Pat. 1,125,259, Jan. 19, 1915.

⁴¹ U. S. Pat. to Ellis, 1,059,720, Apr. 22, 1913.

⁴² Ellis, U. S. Pat. 1,084,203, Jan. 13, 1914.

7; and a catalyser inlet 8 adapted to hold *capsules* of catalyser; 11 is a pump connected with the lower part of the tank by the pipe 12 and having a discharge pipe 13 extending to an inductor 14 which is in communication by means of the inlet 15 and pipe 16 with the top of the treating receptacle 1. From the inductor the pipe 17 extends nearly to the bottom of the receptacle and terminates in a distributor 18 which is so arranged that the flow of material therethrough is both down and angularly against the bottom of the tank or receptacle.

DIRECT MECHANICAL AGITATION

3570. Mechanical agitation of the liquid may be used in combination with gas circulation, oil circulation, with fixed or with suspended catalyst.

3571. Arnold's apparatus ⁴³ is illustrated in Fig. 63. The mixing of the oil with the gas is accomplished by imparting a rotary motion to the oil in the lower

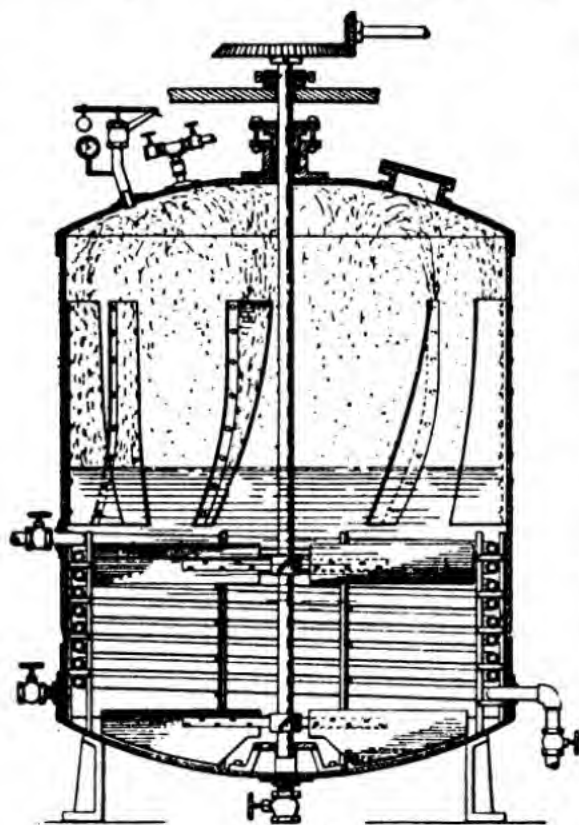


FIG. 63.

portion of the tank and causing the whirling liquid to be thrown upwardly into the space occupied by the gas, by means of fixed blades or deflectors which dip into the liquid. The oil is thrown against the top of the tank, so that it is broken up and showers down through the gas space.

3572. Wells ⁴⁴ has devised an apparatus and process of this type. In a vertical cylinder rotates a central shaft carrying two propeller agitators. The first is near the gas entry at the bottom of the cylinder; this one rotates rapidly and serves to shatter the gas current. The second propeller, placed higher, rotates more slowly and produces a slow circulation of oil, catalyst and gas.

3573. A typical apparatus combining agitation, baffles and oil circulation is described by Lane.⁴⁵ This consists of a vertical cylindrical vessel which is heated by means of a steam jacket or otherwise. Beaters rotating horizontally round a central vertical shaft, alternate with annular sloping shelves on the sides of the vessel, so that the oil entering at the top is alternately sprayed outwards to the sides and guided to the center of the beaters next below, and so on until it reaches the bottom; it is then pumped again to the top of the vessel.⁴⁶

⁴³ U. S. Pat. 1,181,205, May 16, 1916.

⁴⁴ U. S. Pat. 1,1383,887, July 5, 1921.

⁴⁵ Brit. Pat. 968, Jan. 21, 1915; *J.S.C.I.*, 1916, 642.

⁴⁶ See also French Pat. 481,504, Dec. 13, 1916; *Chem. Abst.*, 1917, 2122.

3574. The apparatus described in Lane's U.S. Pat. 1,307,588 of June 24, 1919, is an improvement on that described in British Pat. 968 of 1915, and French Pat. 481,504 of 1916.⁴⁷ The improvement consists in employing internal circulation of the oil instead of pumping it through an external pipe. The apparatus consists of a main cylindrical reaction vessel with the usual connections. In this is an inner cylinder open above. At the bottom of the latter is a centrifugal pump which serves to draw the oil-catalyst mixture from the inner cylinder and to drive it upwards in the annular space so that it overflows at the top into the inner cylinder. In the inner cylinder rotates a central shaft carrying discs with blades; these rotate between annular shelves sloping to central openings.

3575. Calvert claims that improved results are obtained when, in addition to pressure, there are repeated shocks or impacts applied to the oil under pressure. Such a shock, it is alleged, cannot be applied readily by aid of a spray. He subjects a hot mixture of oil and catalyst under pressure and in the presence of hydrogen to such repeated mechanical shocks or impacts. This may be effected by means of rotary beaters. In treating oil for edible use, it is important to avoid decomposition of the fat and Calvert states this can best be done by employing high pressures of hydrogen. Pressures up to and above 250 lb. per sq. in. are used. The mixture of oil and catalyst is supplied to a closed container, Fig. 64, fitted with a propeller at the base and rotary agitators above, in the form of a comb. These rotary or moving parts are mounted on a shaft which is driven by a motor inclosed in a casing over the spherical container. It will be found on trial, Calvert states, that there is a comparatively small

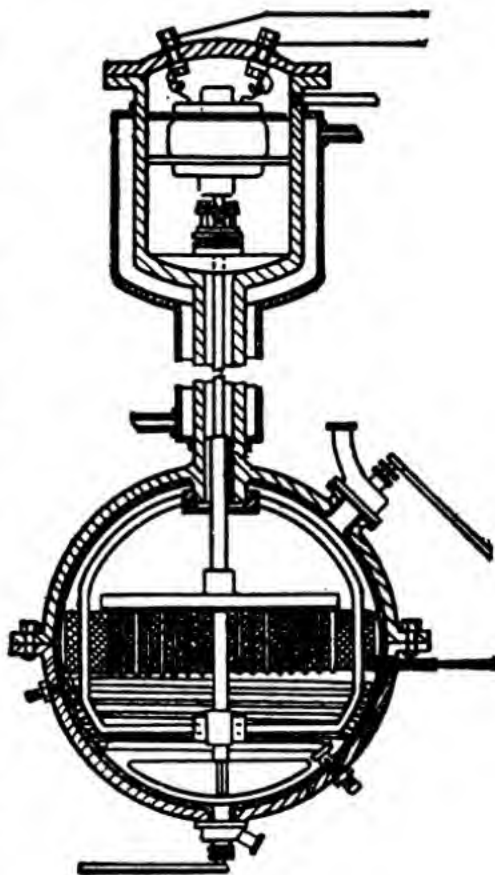


FIG. 64.

range of temperature at which absorption is most active. The curve showing the rate of absorption and the temperature follows practically in a straight line till a certain point is reached, when it ceases to have an upward inclination and passes over into a substantially horizontal line. This curve is indicated in Fig. 65, which is the approximate curve for fish oil. The rate of absorption, as stated, is also increased with the pressure and especially in the case of vegetable oils intended for food purposes the pressure should be high to prevent decomposition. In the latter case the pressure should be above 250 lb. per sq. in., and may be as high as 500 lb. to 600 lb. per sq. in. Whale oil has been deodorized in twenty minutes, and hydrogenated to a hard fat in fifty-five minutes with the Calvert apparatus. The approach of the point of saturation can be readily ascertained by observing the absorption of the hydrogen by a suitable gauge on the hydrogen supply pipe. With this apparatus there is little likelihood of leakage of hydrogen so that the gauge gives a correct indication of the rate of absorption.

⁴⁷ *Chem. Abst.*, 1917, 3122.

3576. Various forms of apparatus are employed by Calvert,⁴⁸ one of which is shown in Fig. 66, and consists of a gas-tight inclosure comprising a commingling chamber *a*, a motor chamber *e*, and a pipe *d* connecting the two. The liquid to be treated such as oil, is placed in the commingling chamber *a*. The commingling means is in the form of stirrer blades *c*

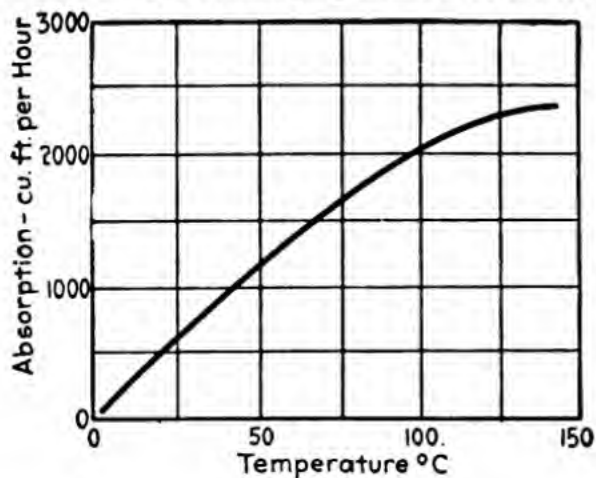


FIG. 65.

mounted on a shaft *b*, which passes through the pipe *d* and is driven by a motor *f* located within the motor chamber *e*. In the case of the hydrogenation of oils *f* is preferably a motor of the induction type so as to avoid sparking. The gas which is to be commingled with the oil is supplied to the gas-tight inclosure by a pipe *g* which for instance may be connected to

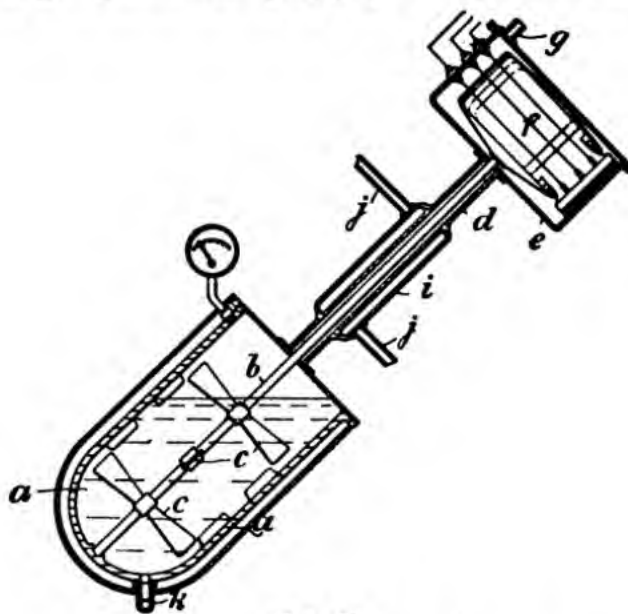


FIG. 66.

the motor chamber *e*, the gas passing from the chamber through the pipe *d* into the commingling chamber *a*. In the hydrogenation of oils this pressure is sometimes fairly high and hence the great difficulty associated with the prevention of leakage if the stirring mechanism for the shaft *b* passes through a stuffing gland. In the apparatus of Calvert there are no pack-

⁴⁸ U. S. Pat. 1,123,092, Dec. 29, 1914.

ing glands for any moving parts passing through the walls of the gas-tight inclosure and consequently hydrogen cannot leak from the interior of the vessel. In order to prevent vapor rising to the motor chamber *c* and to maintain this chamber fairly cool, a jacket *i* through which water circulates may be arranged on the connecting pipe *d*. The finished product is removed from the commingling chamber *a* by a pipe *k*. Another form of the apparatus, Fig. 67, has stirrers driven by an electromagnet placed outside of the hydrogenation chamber. On rotation of the shaft carrying the magnet the stirrers inside the chamber are actuated by magnetic action.

3577. Figure 68 represents this type of oil-hydrogenating apparatus. In the design is embodied the patented principle of enclosing the agitating motor in a

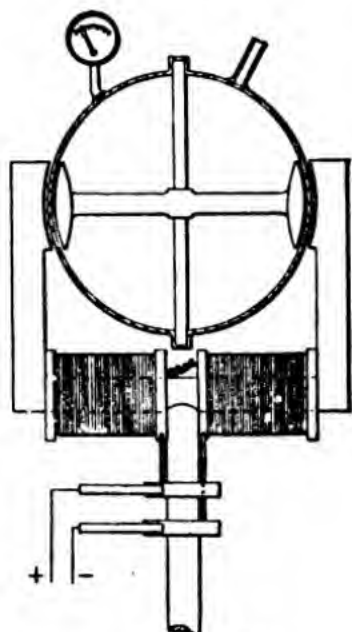


FIG. 67.



FIG. 68.

chamber essentially an extension of the autoclave proper, and under the same gas pressure. By this arrangement the risk of leakage is entirely eliminated, and at the same time high stirring speeds are rendered possible without the frictional resistance which would be caused by shafts passing through glands, etc. The autoclave proper is the lower vessel shown in the illustration, and is enclosed in a heat-insulating jacket. The top vessel contains the electric motor, the intermediate tube through which the stirrer shaft passes being enclosed in a water jacket in the large sizes. Current is conveyed to the motor by insulated screws on the top of the machine. On the right is the flue and the hydrogen feed pipe, the charging and discharging tube being shown on the left. For convenience in discharging the contents, in the smaller sizes the whole is mounted on

trunnions. The oil is brought into a state of fine division by the stirrer blades, which cause the liquid to rotate against the inner side of the vessel, to which perforated baffle plates are fitted. The working pressure is 200 to 250 lb. per sq. in., and the temperature about 185° C., but every machine is tested to 1000 lb. cold water and to 500 lb. gas at 200° C. The illustration represents a small size, suitable for oil laboratories, which stands about 4 feet high, but large units also have been manufactured for working in batteries on a commercial scale.⁴⁹

3578. In another method proposed by Calvert⁵⁰ catalyst is treated with hydrogen in a closed vessel containing a rotating comb-shaped agitator surrounded by a stationary gauze screen, which finely subdivides the oil, while a centrifugal propeller at the base flings the mixture upwards to be beaten and subdivided again.

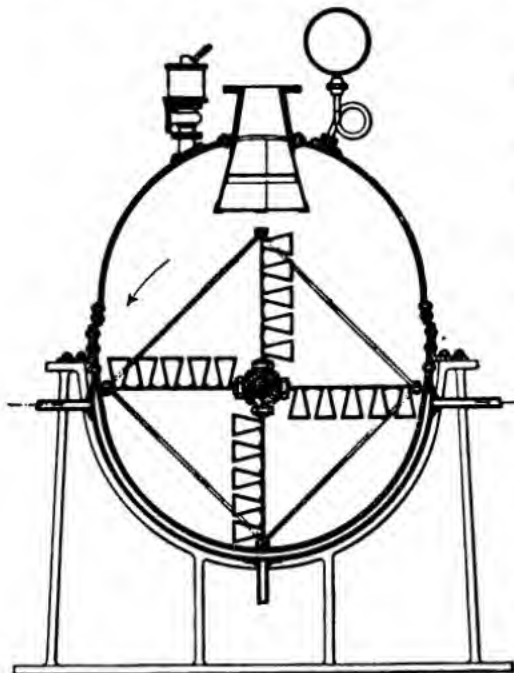


FIG. 69.

3579. Higgins provides agitation by means of beaters or vanes rotating on a horizontal axis. To these arms are attached conical cups, the narrow part next to the arm being perforated, the free base being imperforate. The upper part of the vessel is a gas space. The leading part in the direction of rotation is the perforated narrow mouth of the cup. Fig. 69 illustrates this apparatus.⁵¹

3580. In an apparatus devised by Ellis⁵² and illustrated in Fig. 70 the oil and catalyzer are exposed to an ascending current of the gas. The oil

and catalyzer mixture is caused to circulate in a direction approximately transverse to the direction of flow of the stream of hydrogen.

Apparatus for the purpose is shown in Fig. 70. A treating tank is equipped with a shaft, carrying mixing blades. Hydrogen is entered by a pipe at the bottom and passes out of the apparatus by an exit pipe at the top. The bell-shaped structures on the shaft may be used for the purpose of intercepting the upward flow of the gas, permitting of a longer period of contact. The tank is filled with oil containing catalyzer, finely divided nickel from nickel carbonyl being suitable for this purpose. The stirring apparatus is put in motion and hydrogen introduced.

3581. Allbright⁵³ uses a cone-bottomed reaction vessel. In this is set, centrally, an inner cylinder of relatively small diameter. At the bottom of the

⁴⁹ *Chem. Trade Jour.* 1913, 618.

⁵⁰ *J.S.C.I.*, 1915, 434; Brit. Pat. 5967, Mar. 9, 1914; U. S. Pat. 1,142,668, June 8, 1915.

⁵¹ U. S. Pat. 1,170,815, Feb. 8, 1916; *Chem. Abst.*, 1915, 4; Brit. Pat. 15,063, June 13, 1913.

⁵² U. S. Pat. 1,095, 144, Apr. 28, 1914.

⁵³ U. S. Pat. 1,404,708, Jan. 24, 1922 (first application filed June 28, 1915; renewed Sept. 22, 1920).

inner tube are two propellers, right- and left-handed: thus, though they rotate in opposite directions, they both drive the gas, oil and catalyst mixture upwards through the cylinder, to spill over at the top, through the gas space, into the main body of liquid. The hydrogen is admitted at the lowest point, viz., the apex of the cone. At the surface of the liquid in the outer cylinder are set skimming cups which take off small quantities of the oil, etc., and convey it to a manifold from which it is pumped to the apex of the cone.

3582. An apparatus for hydrogenating oils designed by Sugita consists of a cylindrical hydrogenating vessel or converter which is provided with two revoluble shafts, one within the other. A propeller with a number of nozzles for supplying hydrogen, each provided with an automatic valve, is attached to the end of one of the shafts. By this arrangement the hydrogen is made to contact rapidly and thoroughly with the oil, thereby facilitating the hydrogenation.⁵⁴

3583. Kayser⁵⁵ describes apparatus one form of which is diagrammatically represented in Fig. 71. Here *A* is a closed horizontal cylindrical vessel in which

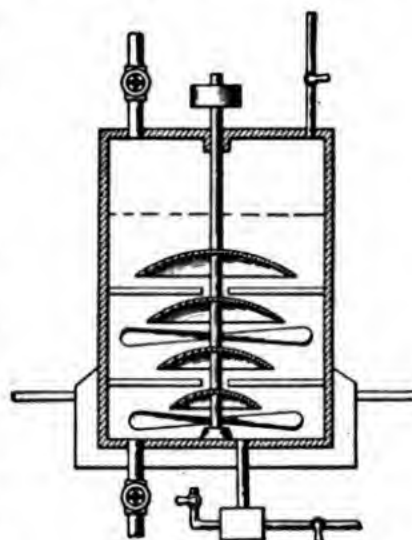


FIG. 70.

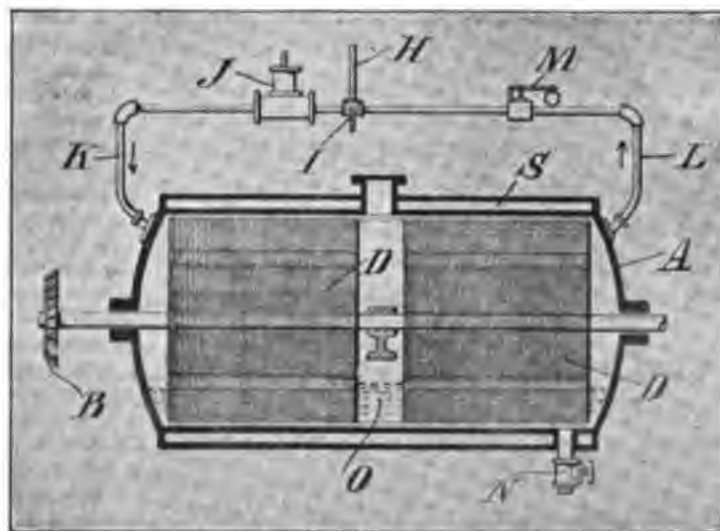


FIG. 71.

is a paddle wheel *D*, made up of blades carrying wire gauze. The paddle wheel is rotated by a driving gear at *B*. In the upper part of the tank is an inlet for

⁵⁴ Japan. Pat. 30,637. Jan. 19, 1917; *Chem. Abst.*, 1917, 2413.

⁵⁵ U. S. Pat. 1,004,035, Sept. 26, 1911.

charging oil and presumably also the catalyzer, the oil being admitted to the tank in an amount sufficient to fill to perhaps one-fourth or one-fifth the entire capacity. Hydrogen is admitted at *H* and passes, by the three-way cock *I*, to the compression pump *J*, going from there to the treating receptacle. At the opposite end of the tank is an exhaust pipe *L*, carrying a blow-off valve *M*, for the purpose of venting the unabsorbed hydrogen. The temperature of treatment is stated to be about 150° to 160° C. Although the claims call for the use of hydrogen under pressure, no working pressures are specified.

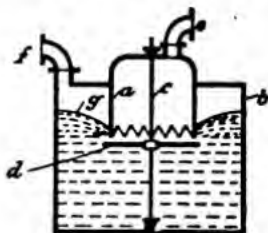


FIG. 72.

3584. Feld⁵⁶ describes an apparatus for causing intimate contact between liquids and gases. A simple type is shown in Fig. 72. Gas enters the stationary bell, *a*, through the pipe *e*, and is distributed through the liquid, *g*, in an atomized condition by the rotation of the agitator, *d*, which also serves to agitate and mix the liquid. Over twenty modifications of the apparatus are described in the specification.

3585. Kimura^{56a} describes an apparatus in which an unsaturated fatty oil, a catalyst such as nickel carbonate and hydrogen gas are agitated in a vertical cylinder enclosed in a steam jacket. The agitator consists of wire frames actuated by a planetary movement.

3586. Pictet hydrogenates oil by causing it to flow by gravitation, with or without the addition of a catalyst, through a series of communicating tubes the walls of which are composed of a catalytic metal. The inner surface of the walls of the tubes is submitted to a preliminary treatment to increase the catalytic activity of the metal. Hydrogen is introduced into the tubes, and the oil is subdivided by rotating devices, which constantly brush against the inner walls.⁵⁷

3587. An unusual method is employed by de Jahn.⁵⁸ Oil is agitated with hydrogen in one vessel and then passed through a second vessel containing the stationary catalyst. The circulation of the fat is continued until hydrogenation is complete. The apparatus used by de Jahn is shown in Fig. 73, the agitating vessel appearing on the right, and the catalyst chamber on the left of the illustration. The catalyst, which may consist of cobalt, palladium, or nickel, is carried in thin layers on an inert material, such as porous burnt clay lumps or pumice stone.

3588. Sieck and Drucker⁵⁹ state that their apparatus is specially designed to accelerate hydrogenation by maintaining the contact between oil, catalyst and gas for a period substantially longer than that usually employed. Essentially this is effected by placing an open-ended cylinder vertically in the center of the reaction vessel. In this cylinder there rotates a continuous helicoidal or spiral propeller, on a shaft which also carries, at the lower end, a propeller of the ordinary type. Between these two propellers is a hydrogen inlet. The action of the

⁵⁶ U. S. Pat. 1,110,914, Sept. 15, 1914.

^{56a} Brit. Pat. 113,232, Aug. 31, 1917.

⁵⁷ *J.S.C.I.*, 1915, 434; French Pat. 472,080, July 24, 1913.

⁵⁸ U. S. Pat. 1,131,339, Mar. 9, 1915; *J.S.C.I.*, 1915, 434.

⁵⁹ U. S. Pat. 1,335,398, Mar. 30, 1920.

propellers drives the oil-catalyst mixture downwards through the inner cylinder, while the hydrogen bubbles upwards in counter-current. See Fig. 74.

3589. Agitation also has been effected by motion of a reaction vessel, containing the oil and catalyst. The vessel may be a drum rotating ⁶⁰ or oscillating ⁶¹ on a longitudinal horizontal axis.

3590. In Ney's apparatus ⁶² the catalyst is placed in baskets in the reaction chamber. In this chamber an oil mist in an atmosphere of hydrogen is produced by atomizers. The catalyst baskets are rotated at a speed such that the centrifugal force is sufficient to throw off the grosser particles of oil while permitting the mist particles to come into intimate contact with the catalyst.

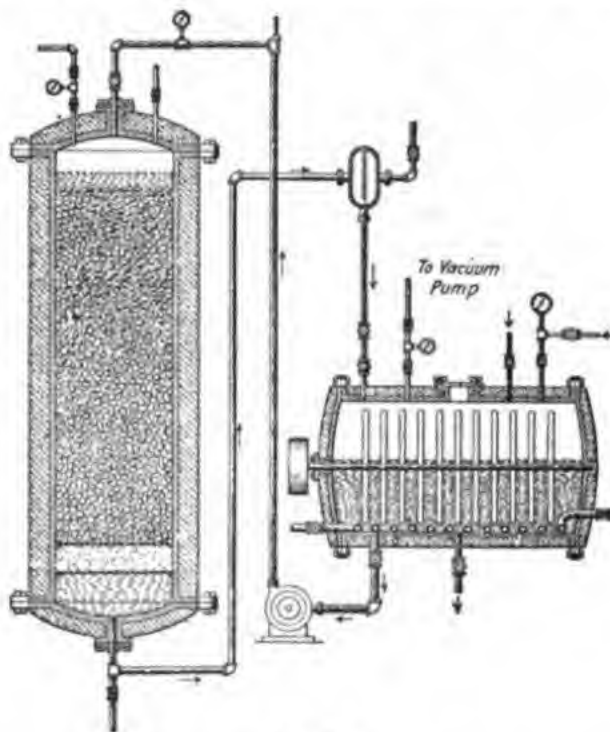


FIG. 73.

3591. A highly complicated system is specified in patents to Blair, Campbell and McLean, Ltd., ⁶³ and to Blair and Ferguson. ⁶⁴ In a cylindrical high-pressure reaction vessel is fitted, centrally, a rotating shaft. From the sides of the vessel there project annular, sloping shelves with central holes. The shaft is fitted with a series of buckets perforated for the passage of bristle brushes. These buckets rotate between the annular shelves. The lower end of the shaft carries a stirring device which maintains the catalyst in suspension. The oil-catalyst

⁶⁰ U. S. Pat. to Ellis, 1,052,469, Feb. 11, 1913.

⁶¹ Brit. Pat. to Charlton, 1,410, Jan. 19, 1914.

⁶² U. S. Pat. 1,185,704, June 6, 1916.

⁶³ Brit. Pat. 144,478, Aug. 28, 1919.

⁶⁴ Brit. Pat. 144,479, June 19, 1919; *J.S.C.I.*, 1920, 551A; *Chem. Abst.*, 1920, 2996.

mixture is pumped from the bottom of the vessel over the first shelf. Flowing through the central opening it enters the first rotating bucket. Flung by centrifugal force along the bristles it enters the gas space as a mist: it collects on the wall, flows down the second shelf to the second bucket, and so on. The later patent describes an inner cylinder with perforated baffles, geared to rotate in the same sense as the central shaft, or in the opposite sense. This cylinder is per-

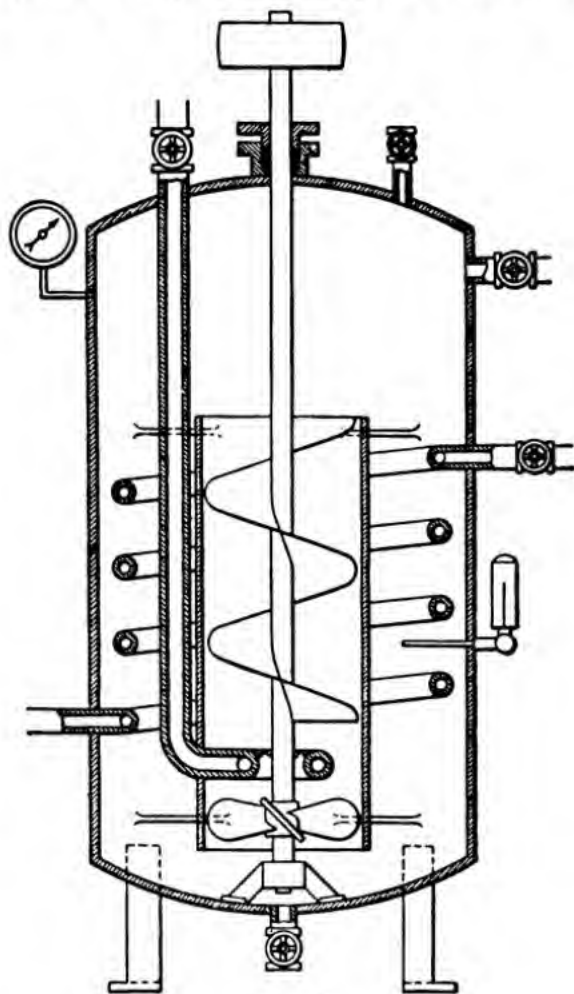


FIG. 74.

forated with openings through which gas enters and is forced against the centrifugal spray of liquid.

3592. The firm of H. Schlinck & Co., of Hamburg, Germany, hydrogenate oil by passage through a centrifuge, the drum of which carries a porous lining supporting palladium catalyzer which offers a frictional resistance to the passage of the oil. Openings are provided in the walls of the drum in which is placed rough or porous material covered with precipitated palladium. Several drums may be arranged in series.⁶⁵

⁶⁵ Brit. Pat. 8,147, 1911; U. S. Pat. 1,082,707, Dec. 30, 1913.

3593. Steward in a long and detailed specification ⁶⁶ describes an elaborate apparatus and method for hydrogenation of liquids. The original patent should be consulted for particulars. Essentially the process consists of producing a film of the substrate (e.g., unsaturated oil) by centrifugal means under conditions permitting control of the film thickness. This film is exposed to the hydrogen atmosphere at any desired pressure and temperature. The catalyst will usually be suspended in the substrate, but it may be fixed. The principal advantages claimed are accuracy of control, rapidity of action, constant freshening of catalyst surface by attrition.

3594. Mechanical agitation of the *catalyst only* is effected by Walter through the application of a magnetic field. If the catalyst itself is not magnetic it is supported on a magnetic body. By rapidly making and breaking the circuit forming the magnetic field, fresh parts of the catalyst can continually be brought into contact with the reacting substances and the catalyst can be moved to different parts of the apparatus. For reactions with gases the catalyst is supported preferably on nets or perforated plates and a magnetic field is maintained permanently near the outlet to cause the settling of any material carried along by the gas.⁶⁷

3595. A combination of several methods is described in a patent to Fujimura and others.⁶⁸ From the bottom of a reaction vessel the oil is pumped to a rotating spraying device at the top. The spray of oil is projected against a gauze screen which rotates, in the gas space and in the oil, in the sense opposite to that of the sprayer. This screen is composed of nickel activated on the surface.⁶⁹ Hydrogen enters by nozzles in the body of the oil which are so arranged as to cause the oil to rotate in the same sense as the sprayer. Here we have (1) agitation by gas current, (2) spraying of the oil, (3) fixed catalyst, (4) mechanical agitation.

3596. A similar combination is used by Walker.⁷⁰ A body of oil to be hardened is placed in a closed receptacle. This oil contains finely divided catalyzer. The receptacle contains a shelf supporting a bed of catalyzer which is placed above the body of the oil. The mixture of oil and finely divided catalyzer is pumped from the bottom of the receptacle to the top where it is sprayed upon the bed of the catalyzer and passing therethrough collects in the body of oil beneath. The latter is stirred by an agitator while hydrogen is blown through the oil. The unabsorbed gas is withdrawn from the top of the receptacle and is passed through a condenser to remove moisture. It is then returned to the bottom of the receptacle. Thus both the oil and the gas are constantly circulated through the oil container.

⁶⁶ U. S. Pat. 1,284,488, Nov. 12, 1918 (application Aug. 19, 1912, renewed June 10, 1916.)

⁶⁷ Ger. Pat. 295,507, Apr. 20, 1913; *J. Chem. Soc.*, 1918, *Abst.* ii, 163; see also French Pat. (to Walter) 471,108, Oct. 15, 1914.

⁶⁸ Brit. Pat. 157, 057, June 14, 1920.

⁶⁹ By treatment with nitric acid, followed by reduction.

⁷⁰ U. S. Pat. 1,276,290, Aug. 20, 1918.

CHAPTER XXXVI

MISCELLANEOUS PROCESSES AND DEVICES FOR OIL HARDENING

3600. There is advantage in increasing the ratio of catalyst to oil because this is one way for shortening the period of working. In suspended catalyst methods this leads to filtration difficulties. Another way of shortening the time and also of lowering the reaction temperature is to work at high pressures of hydrogen. Both these improvements are combined by Ellis ¹ in one method. Fatty oils containing unsaturated components are brought into contact with a stationary catalytic agent whose quantity is materially over 1 per cent (even up to 100 per cent) of the weight of oil which would be in contact with the catalyst at any given time, in the presence of a counter-current of hydrogen at high pressure. Thus no material amount of the metal of the catalyst enters into combination with the fatty acid of the oil because in these conditions the oily material may be cooled to a temperature below that at which objectionable side reactions occur, without interference with the hydrogenation.

3601. Maryott ² dissolves fatty oils or fatty acids in a suitable vehicle, such as alcohol, acetone, ether, petroleum ether, benzene, chloroform, carbon disulphide, carbon tetrachloride, or other fat solvent; and the fat or fatty acid, while in the solvent, is subjected to the action of hydrogen in the presence of some catalyzer, preferably palladium.

3602. It is not necessary that the fatty substance be completely dissolved in the solvent, for triolein, for instance, in alcohol at a temperature below that at which it is completely soluble, is readily reduced in the presence of finely divided palladium. In general, a solution containing about 25 to 50 per cent of fat is preferable.

3603. The process can be carried out in a reaction chamber provided with an agitator and suitable means for regulating the temperature and gas pressure. The solution of the fat or fatty acid in the fat solvent containing in suspension the catalyzer, preferably deposited on some finely divided material as asbestos, is introduced into the chamber, and kept agitated to insure a uniform mixing with the catalyzer, while the temperature is suitably regulated, and the hydrogen conducted into the chamber under appropriate pressure. While the unsaturated fatty bodies, when dissolved, for instance, in alcohol or acetone, are hydrogenized in the presence of finely divided palladium at room temperature under atmospheric pressure, a higher temperature and a greater pressure favor the reduction. After the reduction has proceeded sufficiently far, as shown by tests of samples withdrawn, the mixture is removed from the reaction chamber, the catalyzer separated by filtration, and the solvent distilled off either at atmospheric pressure or at reduced pressure, or without distilling off the solvent the reduced fatty substance may be largely removed by cooling and filtering off the separated fat.

3604. Instead of agitating the solution of the fat or fatty acid in the reaction chamber, the solution containing the suspended catalyzer can be sprayed by means of an atomizer into a chamber of hydrogen, and after sufficient action the mixture can be treated as above for the removal of the catalyzer and the solvent.

¹ U. S. Pat. 1,343,255, June 15, 1922; *J.S.C.I.*, 1920, 551A.

² U. S. Pat. 1,097,456, May 19, 1914.

3605. The influence of the solvent in facilitating the action of the hydrogen on the fat or fatty acid in solution may find an explanation according to Maryott, in the better opportunity afforded for the freer diffusion of the reacting substances. Maryott states that benzene, gasoline, and ether are solvents which greatly increase the speed of the reaction.

3606. A process of, and apparatus for, making lard substitute is proposed by Chisholm.³

Figure 75 shows a casing, mounted upon supports. Centrally and rotatably mounted within the chamber is a catalyzing element, consisting of a spool-like support wound with wire formed of or coated with a catalytic agent, the wound mass being sufficiently porous

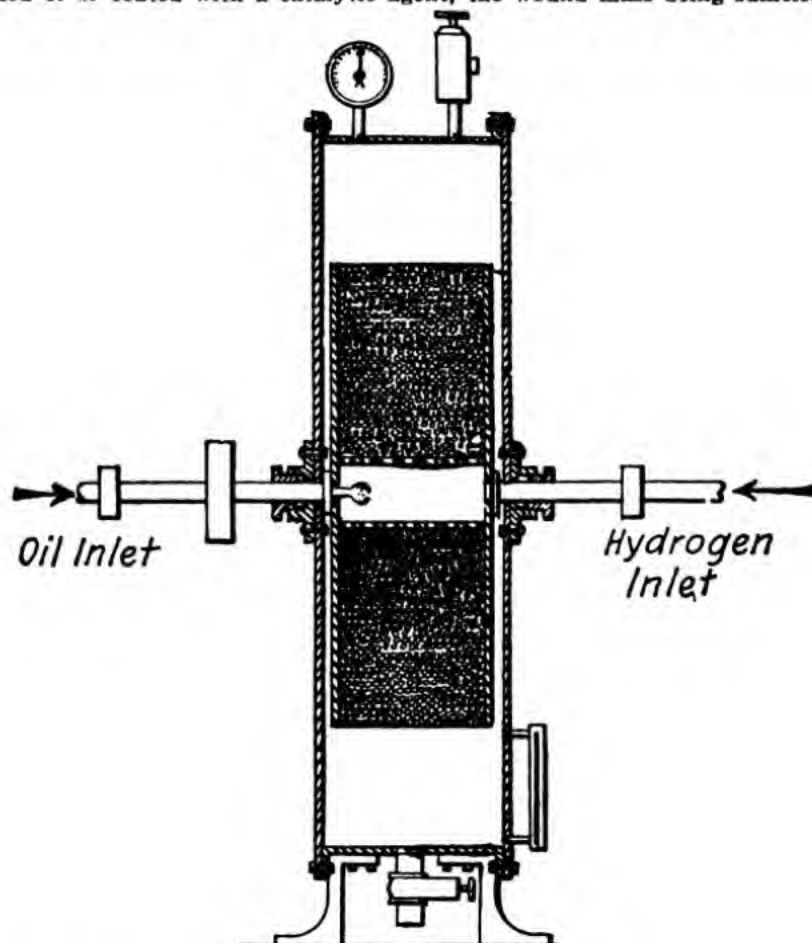


FIG. 75.

to permit of the passage of liquid and gas outwardly therethrough, the liquid and gas tending to follow the spiral course of the wire in its passage outward. In the construction of the catalyzing element, No. 20 copper wire with a rough black unpolished electrolytic deposit of nickel thereon is used. Wire of nickel or palladium which has been roughened also may be employed. Within the spirally wound mass of wire is a central chamber with which there is rigidly connected an inlet pipe to provide hydrogen gas. A pipe on the opposite side supplies oil to the apparatus. The pipes are rotatably mounted within bearings secured upon opposite sides of the casing and the oil pipe is provided with a driving pulley. On being revolved, the catalyzing element moves the oil and gas outwardly along the lines of the spirally wound wire. A temperature in 160° is employed. The hydrogen and oil may be introduced

³ U. S. Pats. 1,113,151, Oct. 6, 1914; 1,114,963, Oct. 27, 1914. *J.S.C.I.*, 1914, 1062, 1168; *Chem. Abst.*, 1914, 3828; 1915, 110.

under pressure. The lard-like fat resulting from the treatment of cottonseed oil in this manner is collected in the lower part of the casing.

3607. The apparatus and method described by Walter⁴ and covered by German patent to him, 257,825 of July 27, 1911, though of little or no importance in the oil-hardening industry, are of potential interest in other hydrogenations as they are specially intended to effect catalytic hydrogenation in the presence of ultra-violet radiation. Figure 76 shows one form of Walter's apparatus.

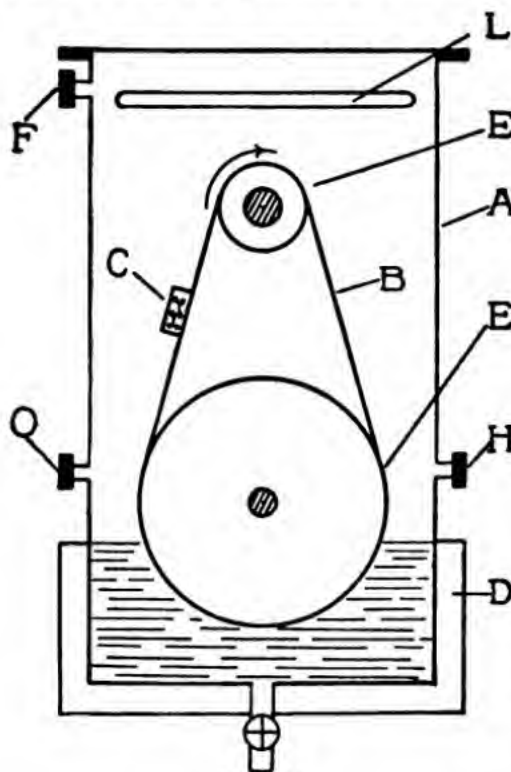


FIG. 76.

3608. A is a closed vessel in which is placed a belt or web-carrying catalyst. The belt may be made of asbestos or cotton cloth impregnated with platinum, iridium, nickel or other catalytic material. The belt is carried on rollers E, one of which dips into the oil. Catalyst also may be carried in the container C attached to the belt B. D is a steam- or water-bath. H is an inlet and F an outlet for hydrogen. O is an inlet for oil. Two other types of apparatus are described: one consists of an upright stationary cylinder jacketed for about one-half the distance. The interior has a shaft with 4 arms upon which the catalyst is carried and revolved through the liquid and gas. A bucket arrangement is also attached to the shaft to throw liquid upon the catalyst.

Another type consists of a jacketed horizontal cylinder with a rotating shaft supporting arms for carrying the catalyst. (Figs. 77 and 78).

3609. The operation may be carried out with the aid of chemically active light for which purpose a lamp-lighting system of actinic character is shown at L positioned in the receptacle A. Walter lays great stress on the rapid absorption of hydrogen by oil or other material exposed in this manner in thin films. He states that although the film of oil on the belt covers the catalyst, and in consequence one would expect the reaction to be hindered by the sealing effect of such a film, yet the liquid and gas react very quickly with one another. The solubility of the gas in the liquid, as well as the physical properties of the latter, he states, do not appear to play any essential part, for the sparingly soluble hydrogen exerts its reducing action apparently just as quickly in a thinly fluid alcoholic quinine solution as it does in a viscous fish oil.

3610. Walter recommends passing the oil through a series of receptacles containing catalyst attached to a belt as described or to an agitator arm. the

⁴ *Seifen. Ztg.*, 1913, 442.

arrangement being such that the oil first enters the receptacle which contains the weakest or more nearly spent catalyzer and after short treatment passes to the next container and so on until finally it reaches the last receptacle where the most active catalyzer is employed.

3611. Page ⁶ maintains the catalyst continuously in a state of high activity by inducing in it electric currents of high amperage and low voltage. To effect this he makes his reaction chamber of dielectric material: around this he places a helix connected with a source of high-frequency, high-voltage electric current. The high-frequency oscillating electromagnetic field so produced induces the revivifying currents in the catalyst. The process may be either batch or continuous.

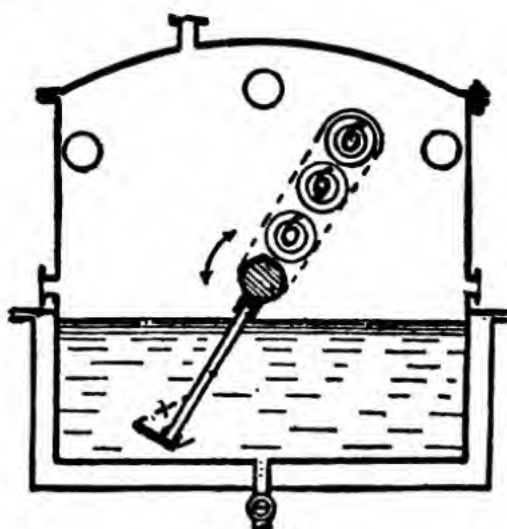


FIG. 77.

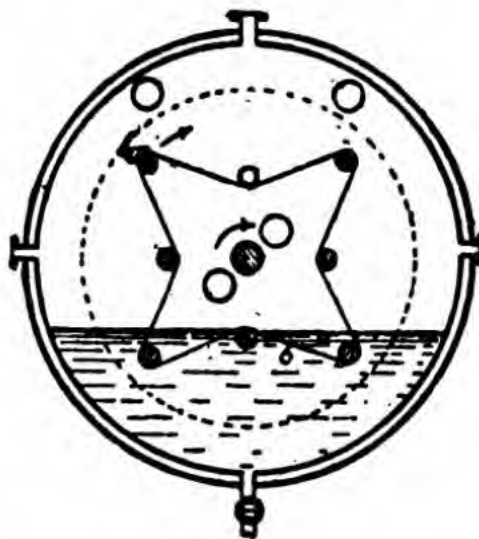


FIG. 78.

3612. The Badische Brit. Pat. 249,309, March 9, 1925, describes a method of refining fat (also mineral and raw oils) by distillation with *non-superheated* steam in presence of an alkali or alkaline earth hydroxide. Hydrogenation of the product is a further step in refining.

REFERENCES

3613. Commercial stearic acid prepared by hydrogenation of distilled esters. U. S. Pat. 1,659,790, Feb. 21, 1928, to Starrels.

3614. Noll. Ger. Pat. 271,641, May 9, 1913; *J.S.C.I.*, 1914, 469. A method of automatic regulation of the supply of liquid to, and discharge of liquid and gas from, pressure vessels in processes involving the mixture of liquid with gas.

3615. Nikaido and Suzuki, Japan. Pat. 35,053, Oct. 4, 1919; *Chem. Abst.*, 1920, 2561. An apparatus for hydrogenating oils. Oil and catalyst are mixed with small bubbles of hydrogen, in a state of emulsion.

3616. Ellis ⁶ discloses an apparatus in which the oil-carrying catalyst (e.g., colloidal nickel) is converted to a fine mist by action of *water-gas*.

3617. An apparatus designed by Winship ⁷ for heating oils with the aid of tubular electrical resistance elements is illustrated in 78a (page 410). These tubular elements are open-

⁶ U. S. Pat. 1,472,281, Oct. 30, 1923.

⁷ U. S. Pat. 1,390,687, Sept. 13, 1912.

⁸ U. S. Pat. 1,712,372, May 7, 1929.

ended and are set vertically in a tank in which the oil is to be heated. The elements are electrically connected in series and may be operated on three-phase, single-phase or direct current. It is shown connected for three-phase current. Porcelain and mica are used as

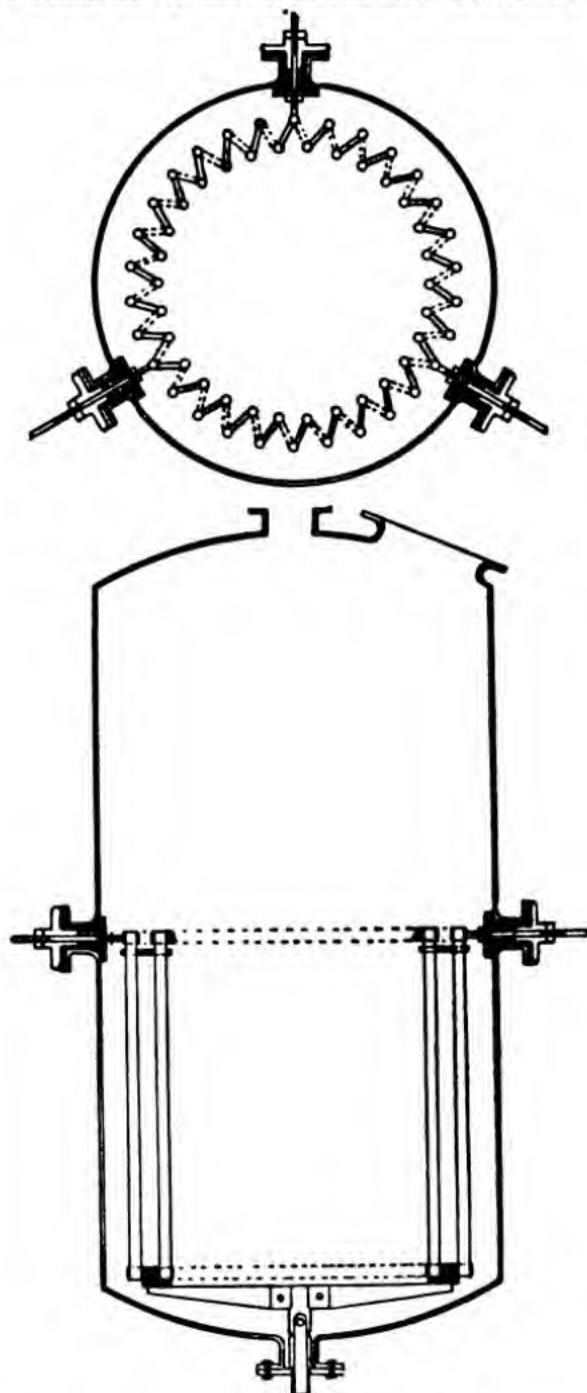


FIG. 78a.

insulation. The effect of the circulation of the oil through the tubes, coupled with the generation of heat over a large area of heating surface, has resulted in the production of oils of an unusually light color. See para. 3516, page 377.

CHAPTER XXXVII

HYDROGENATION OF FATTY OILS

INDUSTRIAL PRACTICE

3700. Whether the plant is to treat animal or vegetable oils, or fish oil, the following general procedure may be laid down for guidance in the equipment and operation of a hydrogenating works.

3701. The starting-point is, perhaps, the preparation of catalyzer. Of course the procedure employed for its preparation depends on the type of catalyzer selected. Suppose nickel be chosen as the active material, to be used on a suitable carrier or supporting base. To this end a solution of a nickel salt, such as the nitrate or sulphate, is mixed in vats with the support, in the presence of a precipitant, or the latter is subsequently added, and the material is well agitated. Soluble salts should then be removed by washing and the material dried. These operations may take place in a filter press supplied with air under pressure. The caked product should be ground in a ball or pebble mill until resolved into a fine powder.

3702. The catalyzer is now ready for reduction, which should be performed with extreme care as the entire oil-hardening process depends on the efficiency of the catalyzer. A simple and efficient type of catalyzer-reducing device is represented by Fig. 79. *A* is a brick structure which contains the reducing drum *B*. The latter is rotated by means of the sprocket *C*. *E¹E²* are stuffing boxes which admit of rotating the drum without disturbing the gas inlet and outlet. The catalyzer is admitted and withdrawn through the gate *G*. The drum is filled about two-fifths full of the catalyzer and hydrogen passed in. When tests for oxygen show that all the air has been expelled the drum is heated to a temperature not exceeding 360° C. During reduction the hydrogen is passed through at a considerable rate in order to remove the steam formed, thus reducing the partial pressure of the latter and facilitating the reduction of the nickel oxide or hydrate. The gases issuing from the exit side of the drum may pass through a water seal and after purification may be returned to the gas holders to be used again. When the issuing gases are found to contain no steam the reduction is complete, the heating is discontinued and the catalyzer allowed to cool in a current of hydrogen.

3703. After cooling the catalyzer, the hopper shown in Fig. 79 is coupled to the flange of the gate *G*. The bottom of the hopper dips below the surface of oil contained in a receptacle beneath. Hydrogen is passed in at the valve *J* and the

air is thereby expelled from the hopper. The valve of the reducing drum is now opened and the catalyzer allowed to fall into the oil, with which it should be thoroughly mixed. Thus the catalyzer is effectively sealed from the air.

3704. This method of abstracting catalyzer from the reducing drum prevents oxidation of the nickel which occurs to a greater or less extent when the catalyzer is withdrawn in contact with the air.

3705. The catalyzer in oil may then be transferred to a large agitating tank in which oil is added in sufficient quantity to make the mixture contain the correct percentage of catalyzer. The contents are thoroughly agitated and transferred to the hydrogenator where the actual hydrogenation takes place.

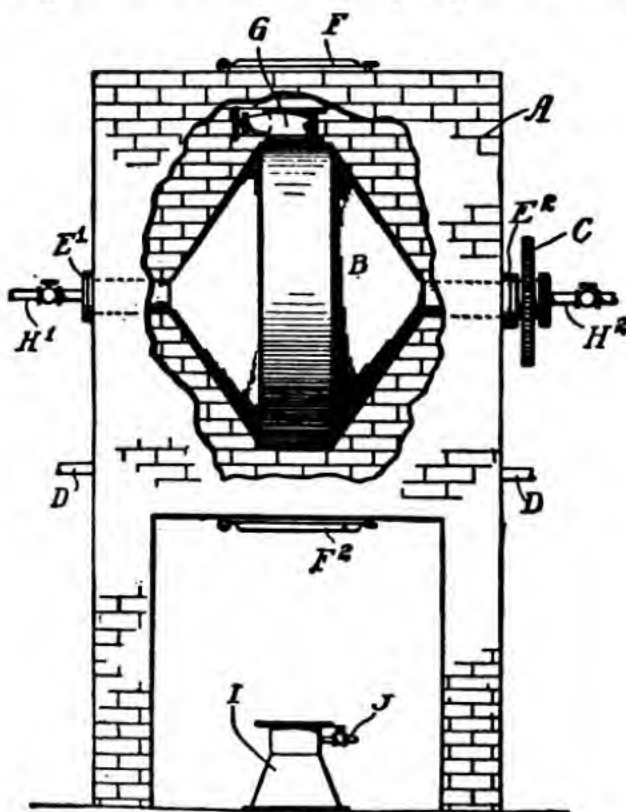


FIG. 79.

3706. Tall iron tanks may be used for this purpose, one type of which is shown in Fig. 80. The air in the hydrogenator is displaced by means of hydrogen and the mixture of catalyzer and oil pumped from the agitator *A* into the hydrogenator *C*. The contents of the hydrogenator are heated to a temperature of 175° to 190° C. by means of superheated steam or hot oil coils, the latter being preferable owing to the danger of leakages of steam into the chamber. The temperature of the contents of the hydrogenator should be registered by means of a reliable thermometer, preferably a recording pyrometer.

3707. The oil and catalyzer in the hydrogenator are circulated by means of the rotary pump *E*, which takes the liquid from the bottom of the hydrogenator

and pumps it through the inductor *I* where hydrogen drawn from the gas space at the top of the hydrogenator is mixed with the oil. *C^K* is a check valve to prevent oil from entering the tank through the suction tube in the event of the inductor suction nozzle becoming flooded. The mixture of oil, catalyzer and hydrogen is ejected through the distributor *D* at the bottom of the hydrogenator. The hydrogen inlet is provided with a safety device *M* and a pressure gauge *P₁*.

3708. The pressure maintained in the hydrogenator is variable according to the oil under treatment and may range from atmospheric or less up to about 25 lb.¹ The difference in the readings of the pressure gauges *P₁*, *P₂* registers the suc-

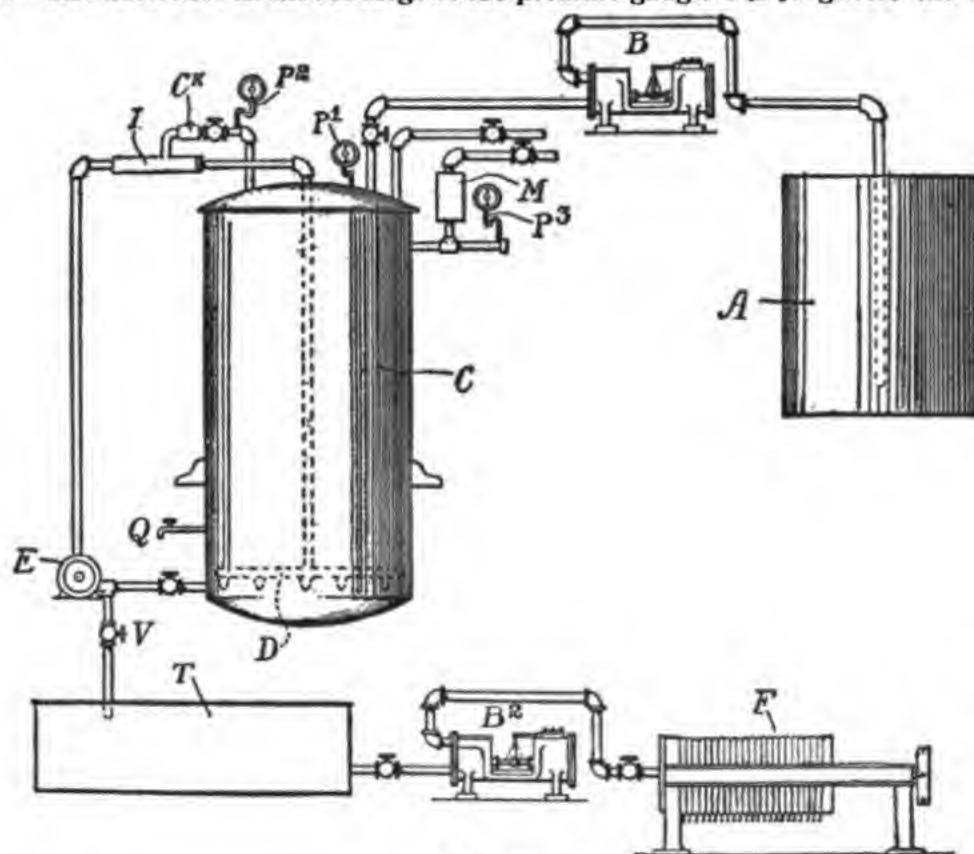


FIG. 80.

tion of hydrogen at the suction nozzle of the inductor. Samples of oil may be withdrawn from time to time from the outlet *Q*. When the sample indicates that the oil has the required hardness the hydrogenator is emptied through the outlet *V* and the contents are run into large tanks which are heated by means of steam coils. From these tanks the mixture of oil and catalyzer is pumped into filter presses where the catalyzer is removed. The oil is finally run into cooling tanks

¹ One of the difficulties met with in the handling of hydrogen has been the loss by leakage of the gas. Under pressure and at a temperature of 150° or 200° C., hydrogen is surprisingly penetrating. Autoclaves with welded seams are desirable for high-pressure and high-temperature work. Moving parts should be avoided as far as possible. A vast improvement has been made during the past ten years in high-pressure hydrogenators.

where it solidifies to a hard fat ready to be made into lard compound, soap or other product.

3709. Of course, the method given above is capable of many modifications, as oils of different character require different treatment and in consequence often-

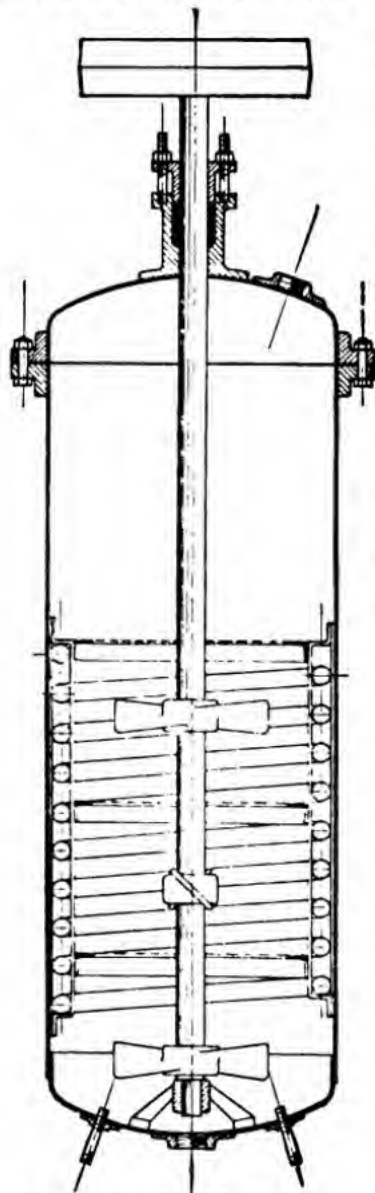


FIG. 81.

times call for equipment which varies considerably from that given by way of illustration. Catalysts vary a good deal in their properties, and conditions which are suitable for nickel in some of its forms will not answer for palladium. A much lower temperature usually suffices when using the latter metal as a catalytic substance.²

3710. A simple type of converter now extensively used is shown in Fig. 81. It consists of a closed tank equipped with a steam coil and stirrer. The vessel is charged with oil and catalyzer and the charge is heated to the requisite temperature when hydrogen is introduced by the small pipes in the bottom of the apparatus. The oil is stirred vigorously during the operation. Heat is developed in hydrogenating fatty oils and when a considerable quantity of oil is being hardened, the heat of reaction may be not only sufficient to maintain the batch at the reacting temperature but may even cause the temperature to rise too high, so that cooling is needed. This is especially noticeable with freshly prepared catalyzer. Sometimes preliminary heating by steam to 100° to 120° C. suffices to start the reaction and the temperature rises rapidly. At 170° to 180° C. water may be passed through the coil to prevent overheating.³

3711. The filtration of oil to remove finely divided nickel, especially when in a colloidal or partially colloidal condition, is aided by the addition of fuller's earth, siliceous earth or some similar bulking material.⁴

3712. Turning now to actual practice, we shall describe three typical plants. The first type uses no mechanical agitation, depending on the current

² Reference is made to the chapters on Catalysts which gives much detailed information on the subject. Attention is, however, called to the existence of several patents covering certain forms of catalytic preparations.

³ In some localities the present tendency of converter design is towards diminishing the diameter and increasing the height. Cf., Brit. Pat. 309,258, Feb. 12, 1928, to Synthetic Ammonia & Nitrates, Ltd. and Rule. This tall converter is for work under high pressures (*Brit. Chem. Abst.*, 1929, 457B).

⁴ U. S. Pat. to Ellis, 1,158,664, Nov. 2, 1915.

of hydrogen to maintain an effective mixture of catalyst and oil: the second plant also uses no moving agitator, but secures the intimate contact of catalyst, oil and gas by means of stationary baffles: in the third plant there is no agitation at all. In one case the catalyst is in powder form and is reduced "dry," and then added to the oil: in another the powder catalyst is reduced in the oil: in the third case the catalyst is stationary and is composed of the surface of nickel turnings first oxidized at the anode of an electrolytic cell, then reduced "dry" in hydrogen.

3713. Method of Preparation of Catalyst. A nickel catalyst with copper as co-catalyst or promoter is prepared as follows: The raw material for making the catalyst is nickel sulphate and copper sulphate, both in crystals. Five parts of nickel sulphate are used to one part of copper sulphate. The crystals are dissolved in hot water and dry soda ash is added to alkaline reaction. After boiling for thirty minutes the precipitate is washed, either by decantation several times, or in a filter press. The precipitate or press cake is dried and ground or is put in a heated ball mill containing steel balls where drying and grinding progress simultaneously.

3714. Alternative Method of Preparing Catalyst. The sulphates of nickel and of copper are dissolved in hot water in a tank fitted with agitators. The tank should not be more than half-filled. To the hot solution are added, first a carrier such as kieselguhr or fuller's earth, then soda ash. The mixture is boiled gently with steam for a brief period. The tank is then filled with cold water and its contents sent to a washing filter press. From this point the method is the same as in paragraph 3713.

3715. The mixture of nickel and copper carbonates (with or without carrier) is placed in a catalyst mixing tank equipped with an agitator. Here it is mixed with oil, and, if necessary with kieselguhr or other filtration aid. The charge of oil is 1 ton.

3716. To a batch of mixed carbonates (prepared by the first method) of 150 lb., 175 to 225 lb. of kieselguhr, fuller's earth or other filtration aid is added. If the carbonate mixture has been made by the second method, it already contains the filtering agent and the weight should be between 300 and 400 lb. The oil and catalyst are agitated in the cold until thoroughly mixed and then a portion is run to a measuring drum.

3717. From the measuring drum 200 lb. of the mixture are blown by hydrogen gas into the hydrogenator. The hydrogenator is already charged with 6500 lb. of oil. High-pressure steam is turned into the steam coils of the convertor to raise the temperature to 180°-190° C. which temperature is necessary for reduction of the nickel and copper carbonates in the oil. Hydrogen is blown through the oil as soon as the carbonate mixture is added. This serves to remove residual moisture therefrom. The hydrogen can be introduced by means of a rotary gas compressor.

3718. Enough catalyst is used to have approximately one-tenth to two-tenths of 1 per cent of nickel in the oil during hydrogenation. Assuming that 5 per cent of the catalyst concentrate blown from the measuring drum into the con-

vertor is nickel, a charge of 200 lb. of this concentrate would give 10 lb. of nickel to the 6500-lb. batch of oil.

3719. The hydrogen leaving the convertor is carried to a scrubbing tower where it meets a spray of caustic soda solution circulated continuously by pump. The purified hydrogen gas does not need drying, the moist gas being satisfactory. A supply of fresh hydrogen from a gas holder insures a constant supply of fresh gas and the gas in circulation is blown off whenever the action gets sluggish. The pressure of the hydrogen in the circulating system is only 3 to 6 in. water-gauge pressure although the pressure employed to blow the hydrogen into the convertor is, of course, higher, dependent on the height of the column of oil. A pressure of 10 to 25 lb. usually is sufficient.

3720. To harden cottonseed oil to the consistency of a lard substitute requires treatment with hydrogen on an average of one and one-half to two hours from the time the temperature reaches 180°–190° C. When hardened to a congealing point of, say, 26°–29° C., depending on the season, the oil is pumped to filter presses where the catalyst is removed. The filtered oil goes to the hardened-oil storage tanks. The catalyst is used repeatedly and, when its action becomes sluggish, the amount is increased until the batch is no longer sufficiently active. The catalyst can be used about a dozen times on a well-refined cottonseed oil.

3721. The oil lightens in color somewhat during hydrogenation, afterwards becoming darkened slightly during deodorizing.

3722. Dry (Roasting) Reduction of Catalyst. This method can be readily used with nickel catalyst, without copper. The nickel carbonate on a carrier (prepared by the second method, para. 3714) from the filter press is run through hoppers into a heated ball mill.

3723. The dried powder is fed from this mill into a horizontal reducing cylinder equipped with a conveying agitator which propels the mass slowly there-through where it is met by a counter-current of hydrogen gas. The cylinder is kept at about 500°–600° C. The temperature is controlled by an electric pyrometer.

3724. The reduced material discharges into oil in a mixing tank. The oil in the mixer is of the same grade as that to be hardened, except when a very poor grade of oil is to be hydrogenated, in which case it is considered advisable to use a better grade of oil for catalyst mixing so as not to poison the latter before it reaches the hydrogenator.

3725. The mixture of catalyst and oil is pumped to a storage receptacle where it is kept agitated. It is run as required into measuring tanks and, when the required quantity of catalyst mixture has entered, the tank is closed and bottom valve opened. Gas pressure is applied which blows the catalyst mixture into the hydrogenator which is being charged.

3726. The catalyst is not added until the main charge of oil in the hydrogenator is heated well above the boiling-point of water. When the temperature reaches 140°–150° C. hydrogen is turned on. Steam is kept on until the temperature is about 180°–190° C. The steam is then shut off and as hydrogenation takes place the temperature rises to 200° C. or higher. At 200° C. for edible oil,

and somewhat higher for soap oil, water is run through the coils to keep the temperature from rising further, otherwise the stock may be discolored. When the oil has reached the proper point of saturation, which can be determined either by index of refraction or by the melting-point, hydrogen is shut off and the oil is passed through cooling coils to the filter presses. As an alternative the oil may be run to a blow tank from which it is pumped to the filter presses. When the press is full it is blown with steam to drive out all the oil possible and it is then cleaned.

3727. Regeneration of Spent Catalyst. Part of the spent catalyst is sometimes used for preliminary treatment of raw oils, especially such oils as contain large quantities of catalyst poisons. The remainder is taken to a tank where it is boiled with an aqueous solution of soda ash and salt, until the oil separates. Steam is then shut off and hot water is pumped into the bottom of the tank to raise the volume to within a foot or two of top of tank. This is then allowed to settle, a clear layer of oil floats on top and the extracted catalyst settles to the bottom. The oil is pumped off and the catalyst and water are pumped through filter presses and roughly washed to remove most of the soap, soda ash and salt. The presses are blown with steam to dry, are cleaned and the press cake removed.

3728. The press cake is next put into wooden tubs with wooden bladed agitators and boiled with an excess of sulphuric acid. The excess acid is essential to secure solution of the nickel from the pores of the kieselguhr. This excess is largely neutralized with soda ash, bichromate of soda is added to oxidize any ferrous iron present to the ferric condition, and then sufficient soda ash is added to precipitate practically all the ferric iron and alumina, but none of the nickel. A test for ferrous iron is made by the ferricyanide method, and for iron and alumina by taking a portion of the green liquor and adding excess of ammonia containing ammonia salts. This should show almost no precipitate.

3729. When the right point is reached the tub is filled with water and the batch filtered. This green liquor, nickel sulphate in solution, is analyzed for its nickel content and then pumped to the original precipitation tubs in proper proportion to replace nickel sulphate crystals.

3730. It is not worth while to recover the nickel still present in the extracted kieselguhr, which is thrown away.

3731. Fat from Used Catalyst. Stiepel⁶ extracted the fat adherent to a spent nickel catalyst which had been used in oil hardening. He found 1.7 per cent gasoline-soluble and 1.5 per cent gasoline-insoluble hydroxy acids. The presence of such a quantity of hydroxy acids Stiepel explains as due to their formation by action of oxygen or water during hydrogenation or, possibly, during steaming out of the press cake. They may act as catalyst poisons.

3732. Butkovski⁶ effects an economy by recovering fat adherent to the spent contact mass. After removal of the nickel from the deposit of catalyst and adhering fat obtained in fat-hardening, the hitherto wasted residue, which amounts to 4 per cent by weight of the hardened fat and contains considerable amounts of kieselguhr from which the fat cannot be recovered by melting, is treated with hot lye (sp. gr. 1.05), 70 per cent of the fat being recovered as soap.

3733. Hydrogenator. A hydrogenator is shown diagrammatically in Fig. 82. It consists of a steel tank supported on four lugs and provided with man-

⁶ *Seifen. Ztg.*, 1925, **52**, 967; *Chem. Abst.*, 1926, **20**, 2758.

⁶ *J. Oil and Fat Ind.*, Moscow, 1926, 11; *Brit. Chem. Abst.*, 1927, 530B.

hole, gas vent, oil fill and drain, coil for heating and cooling and a hydrogen distributor. The hydrogen distributor has four arms and is so constructed that no hardened oil can remain to clog it if the tank is drained and cooled. No agitator

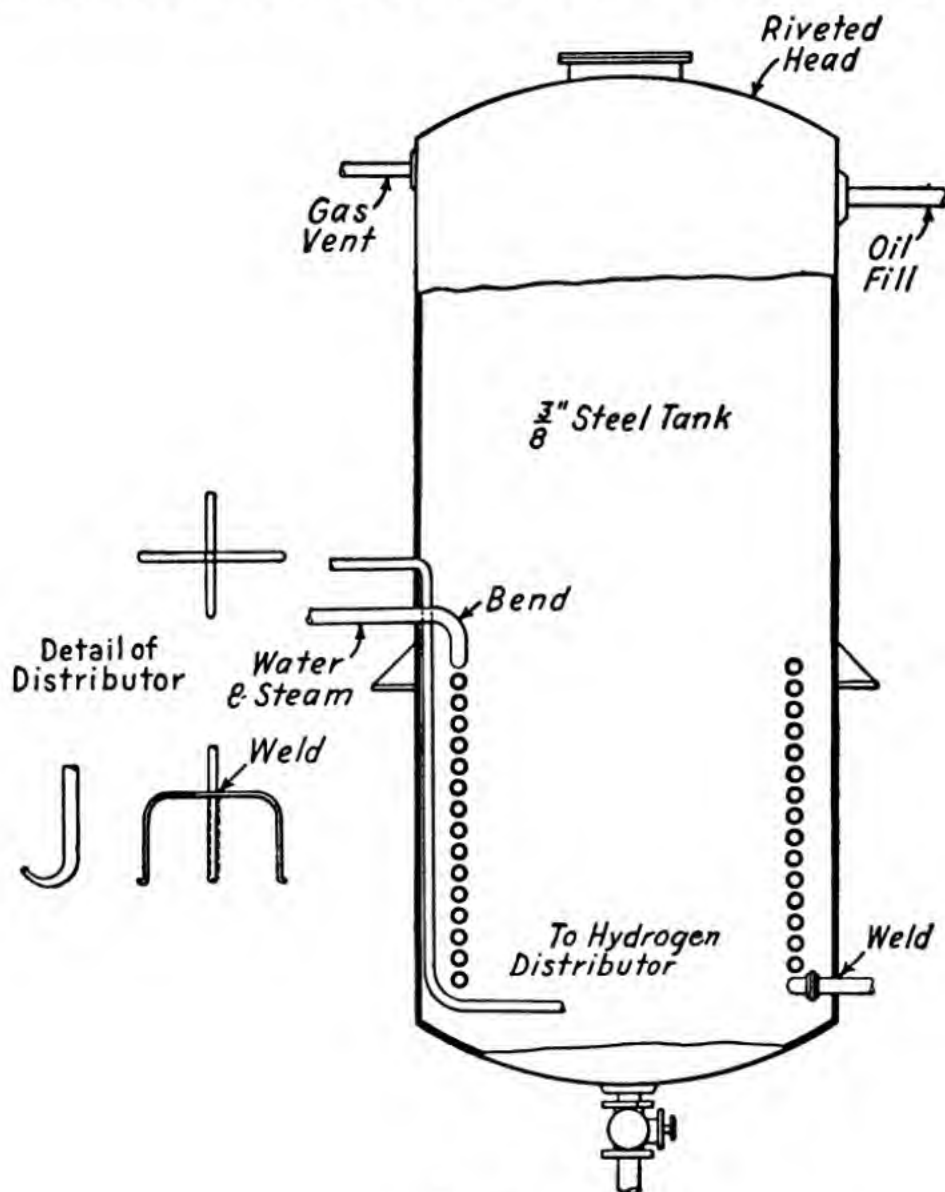


FIG. 82.

is used, and therefore there are no stuffing boxes through which hot hydrogen can escape.

3734. Lay-out. Figure 83 is a flowsheet of this kind of plant.

3735. The Maxted-Thompson Hydrogenation Plant. This type of plant is characterized by a tower, with special baffles, in which the oil and catalyst mixture is vigorously agitated with hydrogen, under a pressure of 4 atmospheres.

3736. The following account is taken from articles by Maxted⁷ and from material furnished by John Thompson (Gas Developments) Ltd., the makers of the plant. The method of and apparatus for preparation of catalyst have been described in paras. 1115 to 1121, pages 131-132.

3737. Preheating the Oil. The Maxted-Thompson plant works at 100°-150° C. according to the nature of the oil under treatment. This low temperature, contrasting with that of 180°-250° C. commonly used, is held to favor the production of a palatable oil. The oil is preheated to this temperature in a vessel shown diagrammatically in Fig. 84. It consists of a cylindrical tank with a conical bottom. *B* is a coil in which high-pressure steam condenses, the latent heat of condensation heating the charge of oil. Uniformity and rapidity of heating are secured by agitation of the oil, either by the small circulating pump *C* or by other means.

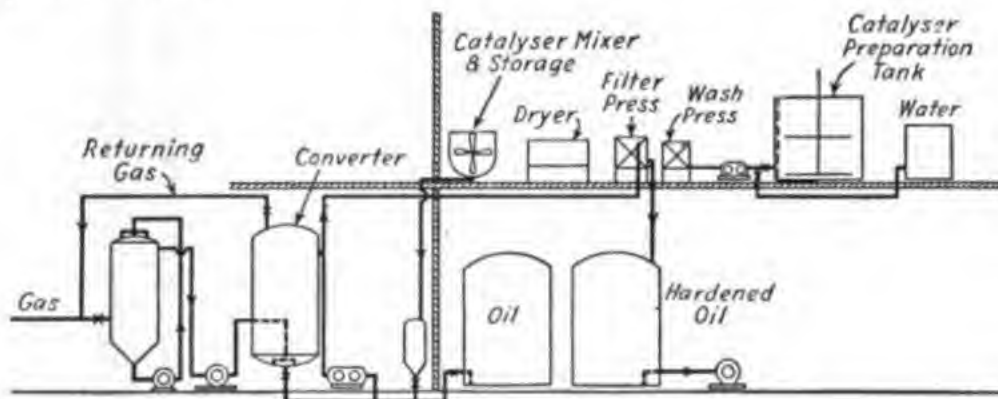


FIG. 83.

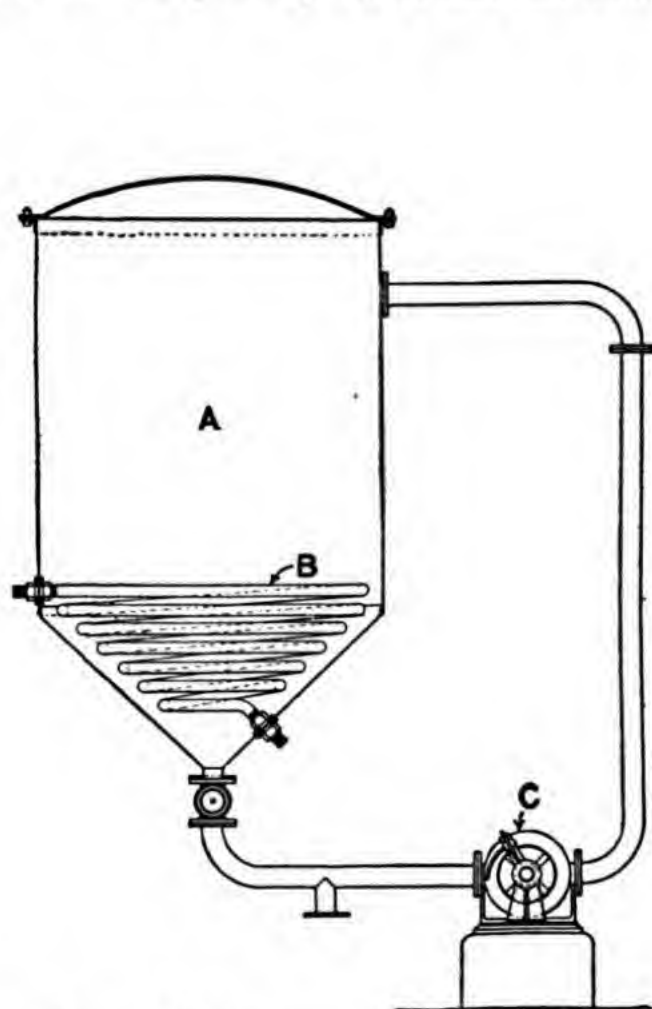
3738. The Hardening Operation. The oil is pumped from the preheater to the hardening vessel where it is mixed with nickel catalyst and treated with hydrogen under slight pressure.

3739. The nature of the hydrogenation vessel will be seen from the photograph reproduced in Fig. 85, and from the diagrammatic sketch shown in Fig. 86. The vessels, which are made in four standard sizes, holding respectively $\frac{3}{4}$ ton, 1 ton, 2 tons and 5 tons per charge, are constructed of welded mild steel. They consist of a central cylindrical portion *A* (Fig. 86) with enlarged ends *B* and *C*.

3740. During the hardening operation, the charge of oil, which in its stationary condition is sufficient to fill the vessel to the oil level shown, is circulated by means of the pump *D* in the direction indicated by the arrow, namely downwards through the vessel and upwards through the external oil circuit. Simultaneously, hydrogen at 40-80 lb. pressure, is circulated in the reverse direction by means of the pump *E*, through the gas circuit shown, namely upwards through the vessel and downwards through the external gas circuit. Hydrogen and oil are thus continuously forced at a high velocity in counter-current to one another through the vessel. The central portion *A* contains a series of specially con-

⁷ *J.S.C.I.*, 1921, 40, 169T.

structed baffles. Each of these consists of a series of radial blades, forming together the propeller-like structure shown in the diagram. The blades in question are curved in such a manner that a substance projected through the column is rotated alternately clockwise and anti-clockwise by successive baffles; in other words, the curve of the series of blades on alternate baffles is right-handed and left-handed respectively. At the same time the form of the baffle is such that a



(By Courtesy of John Thompson [Gas Developments] Ltd.).

FIG. 84.



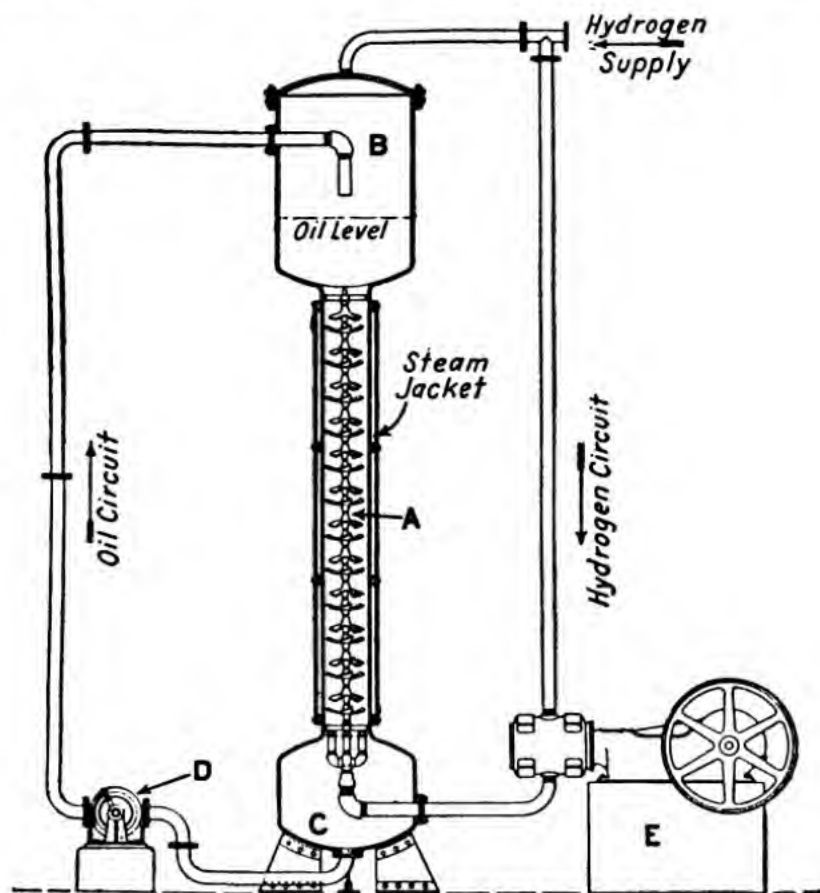
FIG. 85.

substance on being projected through the column is, in addition to the rotation described above, forced alternately towards the center of the column and towards its periphery by successive baffles.

3741. Owing to the high velocity at which circulation is carried out, the speed of the alternate rotations is exceedingly rapid, and a sufficient degree of agitation is obtained for the entire apparatus to be filled with an intimate emulsion of oil and hydrogen. It must be clearly understood that the baffles in question

are fixed, the mixing being obtained by the motion of the oil and of the hydrogen respectively. There are thus no moving agitators, and consequently no stuffing boxes to cause trouble through leakage. The high degree of mixing obtained renders it possible to hydrogenate a charge, for instance of peanut or cottonseed oil, in from fifteen to twenty-five minutes, with an initial temperature of 130°C .

3742. This extremely high velocity and low temperature render the system particularly applicable for the hardening of oils for edible purposes, for which a



(By Courtesy of John Thompson [Gas Developments] Ltd.).

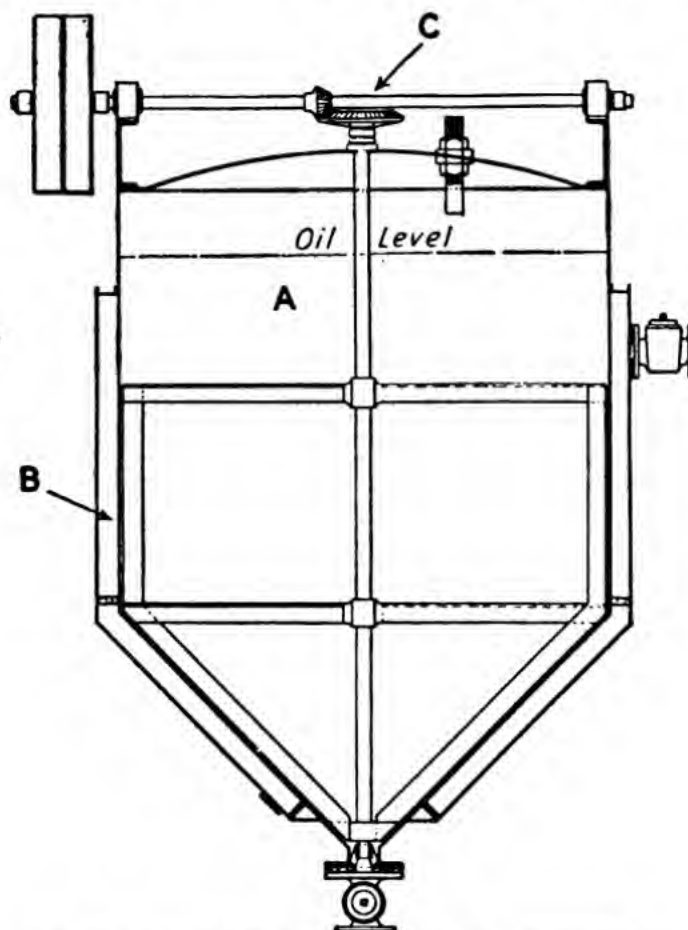
FIG. 86.

product of good flavor is required. The normal pressure of hydrogen is about 4 atmospheres, and fresh hydrogen is supplied continuously to the system during the hardening operation to compensate for that absorbed by the oil.

3743. For controlling the course of hardening, the volume of hydrogen passed into the vessel may be read off from a meter provided for that purpose, and samples are usually taken out from time to time from a small cock. These samples may be filtered quickly through a small filter paper, a small quantity of the filtrate being utilized for determining the change in the refractive index, a property which changes regularly with increasing saturation of the oil: or, more

roughly, a drop from the sample taken is allowed to solidify, the hardness of the resulting fat being estimated by touch. The determination of the iodine value is, of course, in view of the time involved, only of use subsequently.

3744. Subsequent Treatment of the Oil. As soon as the required degree of hardening has been obtained, the charge is pumped into a filtering tank and filtered at a temperature as near to its melting-point as is compatible with con-



(By Courtesy of John Thompson [Gas Developments] Ltd.).

FIG. 87.

venience in working. The hardened oil tank (see Fig. 87), consists of a cylindrical receiver with a conical bottom. Arrangements are provided for the regulation of the temperature, and, where necessary, for the exclusion of air. The oil is, in this tank, maintained in a liquid condition at a suitable temperature above its melting-point, and the stirring gear shown is employed to prevent the separation of catalyst as a sludge upon the bottom of the tank. In the figure, the tank is shown at A. B is a heating or cooling jacket and C is the agitating gear.

3745. From the tank in question, the suspension of catalyst in hardened oil

is passed by means of a filter pump, provided with an adjustable pressure return valve, through the oil filter press, by means of which the catalyst is removed.

3746. The nickel catalyst, thus recovered, is utilized for a further charge of oil, the number of times that a charge of catalyst can be used depending on the nature of the oil and on the temperature to which it has been subjected both during the hardening operation and during filtration. The unnecessary exposure of mixtures of catalyst and oil to the air at high temperatures, in addition to exerting an inhibitive effect on the activity, results in the formation of nickel soap, which renders the filtering of the charge containing it slow and difficult. Under normal conditions, however, the oil runs quite freely through the filter cloth, and no difficulty is encountered in separating the hardened oil, as far as ordinary tests are concerned, in a completely nickel-free condition.

3747. A Continuous Process of Oil Hydrogenation. A process which has attracted considerable attention is one exploited by The Technical Research Works, Ltd., and associated with the names of Bolton and Lush. This is a continuous process. The nickel catalyst is in massive form, consisting of nickel turnings, activated on the surface and enclosed in removable cages. Activation of the nickel is effected by anodic oxidation, followed by reduction in hydrogen. The catalyst is regenerated by removal of the adherent fat with a solvent, followed by anodic oxidation and reduction in hydrogen. A plus pressure of hydrogen is maintained, e.g., 60 lb. The description here given is taken, by permission, from an article by Lush.⁸

3748. The ideal process of hydrogenation would be continuous, would avoid the use of inert supports, and yet use a rigid catalyst, which would remain in the hydrogenation vessel, and would obviate filtration. A rigid catalyst involves the necessity of opening up the plant for its removal, and if this disadvantage is to be minimized, the catalyst must have very high activity to ensure a long life, and its removal from and return to the hydrogenation vessel must be made quick and easy. Moreover, the reactivation of spent catalyst must be cheap and simple, and the method used must lead to complete recovery of activity whatever the nature of the poison including accidental poisons not common to the process. The process of the Technical Research Works, Limited,⁹ lays claim to have approached this ideal. To avoid the use of inert supports, efforts were concentrated on making nickel its own support by the use of a compact form of nickel. A description of the early work in this direction has been published by Bolton¹⁰ and Lush.¹¹ A more recent account of large-scale developments has been given by Bellwood.¹²

3749. The Catalyst. The catalyst consists of pure nickel in the form of turnings or wire, the surface of which is first oxidized and then reduced back to nickel

⁸ *The Industrial Chemist*, June, 1927. In the United States the Bolton and Lush processes are represented by Robinson, Butler, Hemingway & Co., Inc., of New York, who have an experimental plant, capable of hydrogenating 5 tons a week, at Bound Brook, N. J.

⁹ Brit. Pat. 203,218, 1922.

¹⁰ *J.S.C.I.*, 1922, **41**, 384R. See also Bolton, *J.S.C.I.*, 1927, 444T.

¹¹ *J.S.C.I.*, 1923, **42**, 219T.

¹² *Chem. Trade Jour.*, Mar. 6, 1925.

by hydrogen. This form of catalyst avoids the use of an inert support. Further, the catalyst is spread over nickel, and not over an inner core of unreduced oxide, such as may be formed by the reduction of nickel oxide in powder form. Under these conditions, reduction is thorough, and can be carried out at low temperatures. Palmer ¹³ has shown, in a study of the reduction of copper oxide by hydrogen at low temperatures, that reduction takes place at the interface between copper oxide and copper. It is probably for this reason that the surface film of nickel oxide is reduced to nickel by hydrogen at 180° C., or even lower. As Sabatier ¹⁴ has pointed out, the surface oxidation of a catalyst is readily removed by hydrogen at 180° C. Probably the reduction at the interface between metal and oxide is brought about by the nascent or atomic hydrogen formed on the surface of the metal from molecular hydrogen.

3750. Method of Oxidizing the Catalyst. Air oxidation, which requires high temperatures, does not lead to the production of an active catalyst. The method used by Technical Research Works, Limited, is that of anodic oxidation.¹⁵ If a nickel surface is made the anode in an electrolytic bath, using as electrolyte a solution of a salt such as sodium carbonate, which will not allow nickel to pass into solution, a film of nickel peroxide is formed over the surface. Such a thin film is easily reduced, and the resulting catalyst is extraordinarily active. The method has the merits of simplicity and cheapness without sacrificing the important factor of control, since by means of an ammeter and a voltmeter, the conditions of oxidation can be readily standardized, and the production of a catalyst of uniform activity can be depended upon.

3751. Method of Recovering Spent Catalyst. While anodic oxidation is the method employed to oxidize the nickel turnings to produce a catalyst in the first instance, it also serves another and equally important purpose. When the catalyst has been poisoned it is only necessary to extract the oil, and anodic oxidation will remove the poisons so that on reduction a catalyst is formed having its original activity fully restored. Figure 88 shows graphically (Curve I) the fall in activity of a catalyst used in the hydrogenation of whale oil, and the same catalyst restored (Curves II and III) to its original activity by anodic oxidation. In one factory, the same catalyst has been in constant use for four years without loss in either weight or activity, involving nearly a hundred reactivations by anodic oxidation.

3752. Method of Using the Catalyst Cages. Anodic oxidation being the method employed for activating nickel and reactivating spent catalyst, the turnings or wire must be used in a form suitable for treatment in an electrolytic bath. The turnings are therefore packed into cylinders of metal gauze with a center rod of nickel which supports two circular flanges at its extremities. The metal gauze is fastened to the top and bottom flanges. Such a cylinder is called a *cage*. The cages are slipped into asbestos covers, and stood centrally in nickel or nickel-plated vessels giving a 2-in. clearance between the cage and nickel ves-

¹³ *Proc. Roy. Soc.*, 1923A, 103.

¹⁴ *J. Ind. Eng. Chem.*, Oct., 1926.

¹⁵ *Brit. Pat.* 203,218, 1922.

sel. The vessel is filled with a solution of sodium carbonate and a current passed through the electrolytic cell, the cage being made the anode and the vessel the cathode. Earthenware pots may be used with nickel sheet cathodes fitted inside. The strength of the current will vary with the size of the cage. For example, a cage 12 in. diameter and 3 ft. long, holding 100 lb. of nickel turnings, will require a current of 180 amperes and 7 volts for eight hours in an electrolyte consisting of a 5 per cent solution of sodium carbonate. After anodic oxidation, the cages are washed in water, which is frequently changed. The water may be changed automatically by syphon action. In this process, as in the powder process, the importance of washing thoroughly cannot be exaggerated.

3753. A cage construction for holding a catalyst of the nickel anodic oxidation type is also described by Schueler. The nickel turnings are packed around a pipe perforated for the admission of hydrogen. To this pipe are welded spirals of nickel wire which are imbedded in

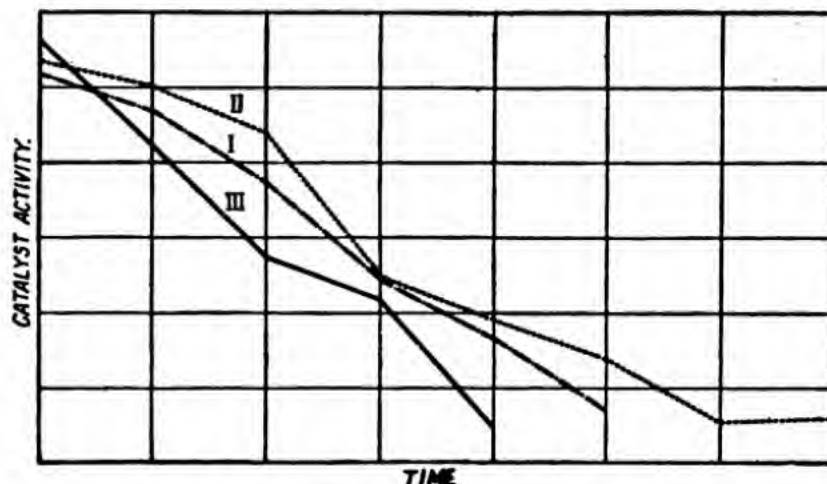


FIG. 88.

the catalyst: these are to ensure adequate contact during the anodic oxidation. The cages are constructed so as to fit together in vertical sets of three, the lowest being adapted to fit on the hydrogen supply casing. The cages are placed in a vertical jacketed cylinder. The oil or other liquid to be hydrogenated is admitted at the top and trickles through the catalyst and meets the up-coming hydrogen.¹⁶

3754. Schueler claims that nickel catalysts made by his process are superior in uniformity to those made by electrolytic treatment of nickel turnings. He uses gauze, rods, strips and other shapes; these are mounted around a vertical pipe which is perforated for hydrogen. The oxidation is effected by hanging the units between cathodes of an electrolytic bath.¹⁷

3755. Lush finds that above a certain minimum rate of flow of oil the hydrogen absorbed per hour is independent of the flow of the oil, or in other words the degree of hydrogenation of the oil as measured by the drop in iodine value is proportional to the speed of the oil passing through the plant.

3756. As cocoanut oil can be hydrogenated to an iodine value of 0.1 per cent

¹⁶ Brit. Pat. 273,045, Apr. 16, 1926; *Chem. Age* (London), 1927, 17, 133; Svizuin uses spirals of iron wire coated electrolytically with nickel. The nickel is oxidized in a caustic bath (*Masloboino-Zhir. Delo*, 1928, No. 3, 25; *Brit. Chem. Abst.*, 1928, 1196A).

¹⁷ Brit. Pat. 274,952, Apr. 28, 1926. *Chem. Age* (London), 1927, 17, 220.

by a single passage through the plant, it has been calculated that all the oil comes into molecular contact with the catalyst.

3757. It is interesting in this connection to note that the hydrogen absorption per hour remains the same whether the final iodine value of cottonseed oil is 70, in which case mostly linolic acid has been hydrogenated, or whether the iodine value is 40, when an equal proportion of linolic and oleic acid has been hydrogenated. This is taken as evidence that the limiting factor in the rate of hydrogenation is the activation of the hydrogen by the nickel.

3758. The effect of the pressure of the hydrogen on the rate of hydrogenation is also interesting. It has been found that the hydrogen absorption is proportional to the square root of the pressure. From this Lush concludes that the nickel atomizes the hydrogen which is then added as such directly to the double bond of the unsaturated oil.

3759. The following table confirms the results previously published, but with a pressure variation of 100 lb. instead of 10 lb. These results are useful in adjusting the working conditions of a large plant. If the flow of oil is too slow the catalyst is not all covered, and the hydrogen absorbed per hour will increase with increased flow of the oil. If, on the other hand, the flow of oil is too fast, in order to reach the nickel the hydrogen must pass through a thick film of oil, and this will determine the amount reaching the catalyst in a given time. Since the solubility of hydrogen in oil is proportional to the pressure, when the flow of oil is too fast, the rate of hydrogenation will be proportional to the hydrogen pressure and not its square root.

EFFECT OF HYDROGEN PRESSURE ON THE RATE OF HYDROGENATION

P. Hydrogen Pressure, Pounds per Square Inch	Iodine Values of Final Prod- uct (original oil 106.2)	Difference	Time in Minutes	Cubic Centimeters of Oil	Hydrogen Absorbed, P.	Hydrogen Absorbed, $\sqrt{P.}$
0	95.6	10.6	5	200	708	272
100	66.2	40.0	5	200	347	372
200	51.1	55.1	5	200	256	377
300	40.8	65.4	5	200	207	370
200	48.2	58.0	5	200	270	396
100	60.3	45.9	5	200	398	425
0	91.2	15.0	5	200	1000	384

3760. These considerations enable a plant to be designed with the correct ratio of oil flow to hydrogen pressure.

3761. The Hydrogenation Plant. Figure 89 shows a 4-in. model of a Bolton and Lush plant. The cages are 4 in. in diameter and 2 ft. 6 in. long, and there are two cages per tube. This plant has a capacity of 5 tons per week of cottonseed oil, hydrogenated to an iodine value of 50. Each cage holds 12 lb. of nickel turnings, from which it can be calculated that the turnings occupy 10 per cent of the total space in the cage.

3762. As nickel is ten times heavier than oil, the weight of oil in pounds equivalent to the cubic capacity of the cage is equal to the weight of turnings used to fill it. For estimating the output from a plant of given size one can therefore use the cubic capacity of the plant expressed in pounds of oil or the weight of turnings. Experience has shown that a plant will deliver cottonseed oil hydrogenated to an iodine value of 50 at an average hourly rate expressed in pounds per hour equal to its own cubic capacity or the weight of the catalyst contained in it. For example, the plant shown in Fig. 89 requires 100 lb. of oil to fill it; the weight of nickel turnings contained in the eight cages is also 100 lb., and it will deliver 100 lb. per hour of cottonseed oil (average iodine value of 50).

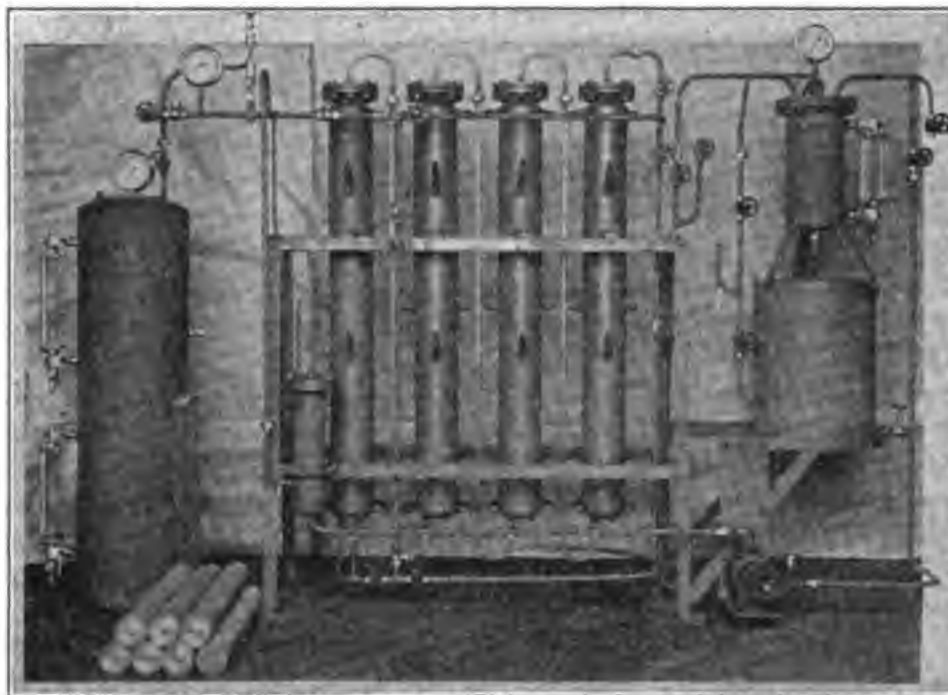


FIG. 89.

3763. Twelve-inch Factory Model. For the hydrogenation of oils in the factory, standard cages each 12 in. diameter and 3 ft. long have been found most convenient. Each tube contains three cages. The first plant was erected in 1922 at the works of Loders & Nucoline, Limited, Silvertown, London.

3764. In this plant the oil is circulated in *parallel* through five tubes, while a sixth is being reactivated. By stopping a tube for reactivation every second day, a uniform output of hydrogenated oil can be maintained continuously with a variation in iodine value not exceeding 1 per cent. The oil from the five tubes flows by gravity down the catalyst in the cages, and collects in a receiver situated below the tubes. It is taken by an oil pump from the receiver and pumped into the tops of the tubes by a suitable manifold connection. The continuous flow of oil is maintained by adjusting an outlet valve from the receiver to deliver the

same volume of hydrogenated oil as is supplied to the manifold by a pump connected to the storage tanks of untreated oil.

3765. Three parallel lagged pipes constitute the heat interchanger between the hydrogenated oil leaving the plant and the untreated oil entering it. This arrangement works satisfactorily for the hydrogenation of cocoanut and palm kernel oils where selective hydrogenation and iso-oleic acid formation do not have to be taken into account.

3766. A strictly continuous process, such as is used in the 4-in. model plant, is preferable for the hydrogenation of cottonseed, soya bean, whale oil, and other oils having high iodine values. The oil is carried from the bottom of one tube to the top of the next by means of the hydrogen, which is circulated round the tubes. This procedure avoids the use of oil pumps between the vessels and, incidentally, by watching the pressure gauges on the tubes one can see at a glance whether there is a free passage throughout the system. The circulation of the hydrogen has the additional advantage that the hydrogen can be passed through coolers to remove water, so that vacuum-drying of the oil entering the plant is unnecessary.

3767. The time taken from the moment the oil enters the preheater or heat interchanger until it reaches the hydrogenated oil receiver is about ten minutes. From here it is forced by the hydrogen pressure in the system—60 lb. per sq. in.—through the heat interchanger to preheat the incoming oil.

3768. In this plant oil is hydrogenated continuously for three weeks, and the plant is then shut down for two days for reactivation of catalyst. After cooling down, the cages are extracted *in situ*, the solvent removed, and the cages taken out and reactivated by anodic oxidation for eight hours in the electrolytic bath. They are then washed, returned to the plant and reduced in hydrogen at 180° C. and hydrogenation recommenced.

3769. The length of time a set of cages will remain active depends upon the nature of the oil and the care taken in refining it, particularly in the removal of soap. In the laboratory common edible cottonseed oil can be hydrogenated continuously for a month by the use of an electrically heated tube provided with a sufficiently large store tank placed above it for supplying the oil by gravity. The apparatus can be left unattended even over the week-ends. Care must be taken by electrically heating the hard oil receiver to prevent the formation of stalagmites of hydrogenated oil which will otherwise rise even over a foot in height and choke the tube.

3770. It is interesting to note the capacity of the activating baths for supplying cages. A set of three earthenware vessels to take the three cages used in each tube will reactivate the cages in eight hours, and since the cages remain active in use from two hundred to four hundred hours, three vessels will supply cages for 25 to 50 tubes where their cages are reactivated in rotation.

3771. The Product. The fact that the catalyst is free from unreduced nickel oxide or kieselguhr perhaps explains why the free fatty acids are not increased by this process. The average free fatty acids of cottonseed oil with an iodine value of 50-55 made in this plant is 0.08 per cent. In the powder process they

frequently rise to 0.5 per cent, or even 1 per cent, with inferior oils where fresh catalyst has to be added to complete hydrogenation.

3772. Lush has previously¹⁸ drawn attention to the importance of encouraging selective hydrogenation and repressing the formation of iso-oleic acid. He considers the effect of the hydrogen pressure on the rate of hydrogenation as evidence of the direct addition of single atoms of hydrogen to the double bond of the unsaturated oil. On this view iso-oleic acid is formed by the single atom being ejected before another atom arrives to stabilize the semi-saturated double bond. If this be so, then conditions which facilitate the arrival of more atoms should decrease iso-oleic acid formation. See Chap. XXXIII.

3773. Experimental evidence suggests that the continuous hydrogenation process described above keeps the catalyst working at its maximum efficiency in supplying atoms of hydrogen. Therefore this process should produce the minimum amount of iso-oleic acid at any given temperature. Figure 90 is reproduced as support to the theory and evidence of the importance of the process to the oil-hydrogenation industry. Hydrogenation by this continuous method may be conducted in two ways: (a) The tubes may be filled and the oil allowed to overflow at a regular rate. This procedure Lush terms the "overflow method." (b) Allowing the oil to drip down the catalyst in an atmosphere of hydrogen so that the same amount of oil is collected in a given time as is yielded by the overflow method.¹⁹ For the second procedure Lush has applied the term "drip method." Lush observes that the complete covering of the catalyst according to the overflow method should be expected to yield greater hydrogen absorption per unit time, but repeated tests made by him show that there was very little difference in the rate of absorption resulting by the two methods, as measured by the iodine values of the resulting oils. He did, however, notice that the overflow method gave oils with a higher melting-point. The difference in physical condition resulting from the differing methods of procedure was investigated and led to the interesting discovery that the course of hydrogenation was different in the two cases. Figure 90, page 437, shows the course of hydrogenation of cottonseed oil by the two methods. It will be noticed that the overflow method gives a conversion of linolic acid to iso-oleic and stearic acids as the main measured change. This manner of conversion Lush observes is normal for hydrogenation with powder catalysts and that very little departure occurs from this type of hydrogenation with variation in conditions of temperature, pressure and mechanical agitation. The graph on the right shows the course of hydrogenation by the overflow method at 180° C. without agitation or pressure. The points marked (X) show the analysis of a sample of cotton oil hardened at 130° C. at 90-pound pressure with very violent mechanical agitation, using a highly active powder catalyst, and it can be seen that the results obtained by the two methods show only small variations in the composition of the mixed acids for such extreme

¹⁸ *J.S.C.I.*, 1923, **42**, 219T. Cf. para. 1052.

¹⁹ In 1914, the Badische Co. advocated the hydrogenation of linseed oil by allowing the oil, in the presence of hydrogen, to trickle over a nickel wire netting carrying a promoter of alumina. See example 4, para. 636, page 59, also para. 637.

changes of physical conditions. Lush notices that at the point where linolic acid disappears the ratio of oleic to iso-oleic acid by the overflow method is almost exactly that found by Moore (*J.S.C.I.*, 1919, 320T) for the ratio of oleic to iso-oleic acid in the hydrogenation of ethyl oleate. The drip method, on the other hand, shows as the main net change the conversion of linolic acid to stearic acid with only a small percentage of iso-oleic acid. This may be arrived at in one of two ways: (1) direct conversion of linolic acid to stearic acid; (2) the conversion of linolic to oleic acid and oleic acid to stearic acid. In view of the formation of iso-oleic acid in the hydrogenation of ethyl oleate, as shown by Moore, and due, as he believes, to the dehydrogenation of the newly formed stearate, Lush thinks it is probable, from these results, that the linolic acid is hydrogenated directly to stearic acid and in the one case—the overflow method—there is momentary absence of hydrogen which has to reach the nickel by solution in the oil and diffusion with the oil for a comparatively long distance, whereby conditions favoring dehydrogenation exist and result in the formation of iso-oleic acid.

3774. The representatives for the United States of the Bolton and Lush processes²⁰ state that the plant has been successfully used for many products other than oils, and even for hydrogenations in the vapor phase. They list the following tried applications:

Tetrahydronaphthalene from Naphthalene, Decahydronaphthalene from Naphthalene, Isopropyl Alcohol from Acetone, Butyl Alcohol from Crotonaldehyde, Butyl Aldehyde from Butyl Alcohol, Thymol from Piperidine, Acetaldehyde from Ethyl Alcohol, Cyclohexanol from Phenol, Methyl Cyclohexanol from Cresol, Aniline from Nitrobenzene and Anisidine from Nitroanisol.

²⁰ See para. 3747, footnote.

CHAPTER XXXVIII

EDIBILITY OF HYDROGENATED GLYCERIDES

3800. A considerable discussion took place in the early days of the oil-hardening industry as to the desirability as foods of hydrogenated fats, in general, and of certain kinds in particular. On the whole the question was resolved in a sense favorable to the new products. Nevertheless, as it is conceivable that the question may again be brought forward at the instance of some vested interest, we retain the record of the discussions to which it gave rise. For details of the controversy the reader is referred to the originals listed or to the abstracts given in the second edition of this book.

3801. Much of the unfavorable criticism, indeed almost all of it, came from Germany. It was based on three objections: (1) The presence of nickel in hardened oils. (2) Doubts as to the inherent suitability of hardened fats for food. (3) Esthetic considerations based on the use as raw material of whale oil and other oils prepared in conditions of uncleanness.

3802. It is true that nickel, derived from the catalyst, can be detected in hardened fat, not always but sometimes, and more often and in larger quantity in fats not intended for consumption as food than in edible fats. With present-day methods the quantity present in the latter class of fats is infinitesimal and opinion is now all but unanimous that it is entirely harmless. When the exquisite delicacy of the dimethylglyoxime test for nickel is considered, the presence of a barely detectable trace will be recognized as devoid of importance.

3803. Apart from carelessness the cause of the presence of nickel in the finished fat seems to be the formation of nickel soaps from free fatty acids of the oil.¹ The difficulty of economically removing these soaps from edible fats is considerable. Their formation is therefore sometimes prevented. One method of doing this is by esterification of the free fatty acids.² In practice, however, alkali-refining is usually the method of choice. This is a routine process in refining edible oils and therefore need not be detailed. It consists in heating and agitating the raw oil with the calculated quantity of alkali, separating and washing the oil. The extracted free acid (as sodium salt) with the intermixed oil, etc., is used as soap stock.

3804. The occurrence of nickel in food is widespread and is due, not only to the use of hydrogenated fats, and to the natural occurrence of the metal,³ but

¹ Bömer, *Zeit. Nahr-Genussm.*, **1912**, 104, and *Chem. Rev. Fett. u. Harz Ind.*, **1912**, 221.

² See paras. 562 to 565.

³ Cf., paras. 3446 and 3447.

also to the use of nickel vessels in the manufacture or in the domestic preparation of food.

3805. The investigators named in the footnote ⁴ have examined this matter. The result of their work is that the quantity of nickel taken up by food from nickel vessels is larger than that found in properly prepared hydrogenated fats and that, even so, it is harmless.

3806. The quantity of nickel found in 1 kg. of food cooked in nickel vessels is tabulated below:

(Ludwig)	Milligrams	(Lehmann)	Milligrams
Spinach.....	25-27	Beef and bouillon.....	26-64
Peas.....	12-16	Potato pulp (equal part of water)	26-40
Lentils (acid).....	35	Spinach.....	22.4
Lentils (boiled).....	24	Damson plum mixture.....	13.3
Sauerkraut.....	54-129	Sauerkraut.....	18-57
Plums.....	35	Fruit cooked in 2 per cent acetic acid solution.....	65-67
		Water, salt water, flesh extract and milk.....	3.5-5.3

3807. Normann and Hugel found:

	Duration of Cooking, Hours	Milligrams of Nickel in 1 Kilo of Material
Coffee.....	$\frac{1}{2}$	0.03
Apple.....	$\frac{1}{2}$	46.0
Cabbage.....	$\frac{1}{2}$	83.0
Red cabbage.....	1	67.0
Sauerkraut.....	$1\frac{1}{2}$	127.0
Kohlrabi.....	1	19.0
Potato.....	$\frac{1}{2}$	80.0

3807B. Solubility of Metals in Milk.^{4a}

LOSS IN WEIGHT OF METAL PER SQUARE DECIMETER EXPOSED TO MILK FOR 30 MINUTES

Temperature °C.	Nickel Mg.	Temperature °C.	Nickel Mg.
20	0.86	75	6.54
30	1.22	80	6.54
45	3.442	85	5.17
55	4.31	90	3.442
62.8	5.85	95	1.22

⁴ Normann and Hugel, *Seifen. Ztg.*, 1913, 959. Ludwig, *Osterr. Chem. Ztg.* (Vienna) 1, 1898; Lehmann, *Arch. für Hygiene*, 1909, 68, 421; *idem*, *Chem. Ztg.*, 1914, 798. Gheorghin, *Ber. pharm. Ges.*, 1914, 24, 303; *Chem. Abst.*, 1915, 487. Vuk, *Z. Nahr.-Genussm.*, 1914, 28, 103; *Chem. Abst.*, 1915, 109.

^{4a} Quam, *Ind. Eng. Chem.*, 1929, 21, 703.

3808. Of seven samples of hardened cottonseed oil examined, four samples contained 0.03 mg. of nickel in 1 kilo. One sample showed a relatively high content, 0.075 mg. of nickel; while the remaining samples contained 0.02 mg. of nickel. Palm kernel oil showed a content of nickel ranging from 0.017 to 0.1 mg. of nickel per kilo, averaging around 0.02 mg. Thus it will be noted that the nickel content of these fats is only about one-thousandth part of that found in foods prepared in nickel kettles, and when one considers that fats generally are not used for edible purposes, *by themselves*, but simply as additions to other foods, the amount of nickel furnished by hydrogenated fatty material amounts to so very little that the consumption of such food year in and year out may be regarded as harmless.

3809. Even in fats intended for technical purposes, the amount of nickel is small as compared with that found in the food materials above-mentioned, as for example:

	Nickel in 1 Kilo, Milligrams
Hardened fish oil.....	3.3
Hardened fish oil.....	1.2
Hardened fish oil.....	3.2
Hardened cottonseed oil.....	0.85

3810. The second objection to the use of hardened oils in food, that based on their supposed inferiority to natural fats in digestibility and availability, has been conclusively disposed of by the daily experience of millions, as well as by laboratory experiments *ad hoc*.⁵

3811. It is evident that a product of wax-like hardness, such as a fully hydrogenated stearin, is not suitable for use alone, as a food fat. It is, however, inconceivable that such a product would be offered for that purpose. Mixed fats, whether produced by hydrogenation to a lard or butter consistency, or by the mixture of a hardened fat with a soft or liquid product are as assimilable as natural fats of the same consistency.

3812. In the process of hydrogenation, not only is hydrogen added to the unsaturated fatty acids, but objectionable and unstable substances are removed by the stream of gas. This confers on hydrogenated oils a high degree of stability which has been positively established by a number of workers.⁶

3813. The keeping properties of some hardened oils examined by Knapp (*Analyst*, 1913, 102) were found to be remarkably good. Although prepared nearly a year and a half previously, and having often been exposed to damp air, yet these samples showed no signs of rancidity. The acidity (0.7 per cent as oleic acid) did not appreciably change during the period of observation. This opinion of the stability of hydrogenated oils is now general. Leimdorfer,⁷ however, found that, even in a vacuum, hydrogenated fats change in color and in odor. This is true of some partially hydrogenated fish oils and not of carefully prepared edible hydrogenated oils.

3814. Ueno and others⁸ found that hydrogenated olive oil, cottonseed oil, cod-liver oil, peanut oil, soya-bean oil, sesame oil and cocoanut oil were superior to the untreated oils, as food materials, because of their greater stability and because of the removal of obnoxious constituents. They state that, under their conditions of working, Vitamin A is conserved.

⁵ Lehmann, *Chem. Ztg.*, 1914, 798, Cf. "Gehartete Pflanzenfette in der Speisefettindustrie." *Seifen-Fabrikant*, 1914, 181; Pekelharing and Schut, *Pharm. Weekblad.*, 1916, 53, 769; *Chem. Abst.*, 1916, 2758; Thoms and Muller, *Arch. Hyg.*, 1915, 84, 56; *Chem. Abst.*, 1915, 1642; Holmes and Lang, *Bulletin No. 469*, U. S. Dept. of Agriculture. Erlandsen, Fridricia and Elgstrom, *Tidskrift Kem.*, 1918, 15, 109; *Chem. Abst.*, 1918, 1793 (this last article deals with experimental and mass feeding, under careful supervision, of a margarine containing 22.8 per cent of fat from hydrogenated whale oil.

⁶ Holmes and Lang, *loc. cit.*

⁷ *Seifen. Ztg.*, 1913, 1317.

⁸ Ueno, Yamashita, Ota and Okamura, *J. Soc. Chem. Ind. Japan*, 1927, 30, 378.

3815. Gill⁹ discusses the subject of hardened oils in their various applications. Concerning edible products obtained by hydrogenation, he observes that it is claimed for them that they can be heated hotter (to 455° F.) without smoking than ordinary fat: this cooks the outside of the food more quickly and prevents the grease from soaking in. Consequently it is less greasy, more digestible, dry and crisp. Another advantage is that no odor is absorbed; fish, onions and potatoes can be cooked successively in the same fat. Another claim is that one-fourth less is used of these fats than of butter; further that it is all fat, while butter contains 5 to 16 per cent of water.

3816. The fight for and against the use in food products of hydrogenated fats made from marine oils was far more vigorously waged than that based on the other objections. For details we again refer the reader to the second edition of this work and to the original papers listed in the footnote.¹⁰ A plea was made by German manufacturers of margarine for the prohibition of hydrogenated whale oil in margarine.¹¹

3817. The tumult and the fighting died when Germany, under pressure of the allied blockade, was in dire need of solid fats. Considerations which, after all, were based chiefly on esthetic grounds gave way before the stern arbitrament of war. Moreover, the processes of winning whale and marine oils have been greatly improved. The fleets are now accompanied by a steamer which is a floating oil refinery. Every effort is made to obtain the maximum of No. 1 oil. Since 1906 the production of whale oil has increased greatly, even alarmingly, for these huge sea mammals are few in numbers, not prolific and are slow of growth. Unless concerted international action is soon taken to protect the whale, the question of the use of whale oil, for any purpose, will become a dead issue, by extinction of the source.

3818. Hydrogenation and Vitamins. The two important vitamins of oils are the vitamins (or groups of vitamins) known as A and D. D has been found in quantity only in marine liver oils, especially cod-liver oil. Both these vitamins are far more resistant to heat than was once thought.¹² But they are very sensitive to oxygen. In industrial methods of hydrogenation it seems impracticable to exclude oxygen altogether. Therefore commercial hydrogenated oils contain little or no vitamin. This is of minor importance because they are not used alone as articles of diet. Butter substitutes are churned with soured skim milk and receive from this source a certain quantity of Vitamin A.¹³

3819. Vitamin Concentration. Funk and Dubin¹⁴ have availed themselves of the stability of Vitamins A and D in hydrogenation conditions at relatively low temperatures to devise a method of concentrating the vitamins of cod-liver oil. The oil is emulsified with a gum-protected palladium catalyst and treated

⁹ *Science Conspectus, Mass. Inst. Tech.*, 1915, 5, No. 4.

¹⁰ Bohm, *Seifen. Ztg.*, 1912, 1087; Lieber, *ibid.*, 1188; Keutgen, *ibid.*, 1914, 89; Offerdahl, *Ber.*, 1913, 559; *Halbmonatschrift f. d. Margarinindustrie* (Düsseldorf) editorial reported in *Seifen. Ztg.*, 1914, 30; *Deutsche Margarine Zeitschrift*, *ibid.*, 118; *Mölkerei Ztg.*, 1913; Klimont and Mayer, *Z. angew. Chem.*, 1914, 27, 645; *J.S.C.I.*, 1915, 148.

¹¹ *Seifen. Ztg.*, 1914, 604; *Margarine Industrie*, 1914.

¹² Funk and Dubin (U. S. Pat. 1,629,074) heat cod-liver oil with glacial acetic acid under reflux for one hour without substantially impairing the vitamin activity.

¹³ About half the Vitamin A content of milk passes into the skim milk.

¹⁴ U. S. Pat. 1,649,520, 1927.

at 60° C. until completely hardened. The vitamins are then extracted from the solid fat.

3820. There are many persons, whole races in fact, who, on religious, hygienic or esthetic grounds, will not eat animal products. Others must eat food of animal origin only when it has been prepared in some ordained fashion and when it contains no forbidden fat. To such persons the oil-hardening industry has been a godsend. Now they can procure sweet fats of any desired consistency without the slightest risk of transgressing their personal or religious rules. In the East an immense quantity of clarified butter (*ghee, samn*) is used in the preparation of food. For this expensive luxury, or quasi-luxury, partially hardened vegetable oil has proved an acceptable substitute. The consumption of this product, of foreign¹⁶ or domestic origin is continually increasing.

3821. The Bureau of Animal Industry requires only that the true nature of hydrogenated fat be stated on the label, e.g., "*Stearine made from cottonseed oil*," showing that it is not the natural article.

3822. Oil Hydrogenation in Italy. An oil-hardening plant has been erected at Brescia by the S. A. Stereol near the electrolytic plant of Soc. Elettrochimica del Caffaro, utilizing the hydrogen by-product of the latter company. The hydrogenation plant is designed to produce 5000 tons yearly of hydrogenated marine oils. Tariff exemption on marine oils for hydrogenation has been granted. Another application of hydrogenation in Italy is contemplated for the treatment of olive oil foots. Hitherto the catalyst poison from the residual solvent has hindered this development. New solvents are now used which are free from this disadvantage.¹⁶

¹⁶ In 1927 India imported 22,222 tons of "vegetable ghee," according to the Prospectus of Oil Products and Butterin Co., Ltd., a company formed to manufacture oil products in India.

¹⁶ *Cotton Oil Press*, 1928, 11, 25.

CHAPTER XXXIX

FOOD PRODUCTS MADE WITH HYDROGENATED GLYCERIDES

3900. Since the addition of less than 1 per cent of hydrogen sufficed to convert cottonseed oil or other vegetable oils into a fatty body of at least the consistency of lard, it followed that manufacturers of ordinary lard compound (that is to say, a mixture of about 85 to 90 per cent of refined cottonseed oil and 10 to 15 per cent or so of oleo-stearin) were attracted by the possibility of producing compound from a "self-thickened" cottonseed oil. Even though there may exist no marked price differential between oleo-stearin and hardened cottonseed oil, yet when, as is the case, millions of pounds of lard compound are made monthly in this country, a reduction in cost of but a small fraction of a cent per pound means an important gross saving.

3901. By the hydrogenation process a lard substitute may be prepared in two ways. The entire oil may be simply hardened to the consistency of lard, care being taken to employ an oil as nearly neutral as possible to prevent excessive solution of catalytic metal, and to avoid a high temperature of treatment so as not to impair the flavor of the product. If the color and flavor are detrimentally affected, resort may be had to a further treatment with fuller's earth followed by steam-vacuum deodorization. The addition of a small amount of cocoanut oil benefits the flavor.

3902. The other method is that of making lard compound which, as indicated above, involves thickening a large proportion of normal oil with a small amount of a relatively hard hydrogenated product. This may be carried out as follows:

3903. After the oil has been hardened, it is freed of catalyzer and then may be run into tanks containing the requisite amount of deodorized cotton oil (or other edible oil) and if necessary the mixture is further clarified and filter-pressed. With hardened cotton oil of 58 to 60 titer, only 7 to 10 per cent is required to thicken the oil to the consistency of lard, although in hot climates a somewhat larger proportion may be needed.¹ The mixture is run on to a chill roll to cause rapid solidification and after slight aeration to improve the color is ready to be packaged. Figure 92 shows a chill roll or lard cooler of the type usually employed.

3904. In this illustration the large upper cylinder or roll is chilled by the circulation of brine and is slowly rotated say from 6 to 10 r.p.m. The hot liquid

¹ An object in making lard compound is to use as large a percentage of cottonseed oil as possible and yet fulfil the required conditions as to the stiffness of the material to withstand warm temperatures without much softening. Compound which stands a moderately warm climate can be made with even as low as 6 to 7 per cent hardened oil.

compound at a temperature of 50° to 55° C. is run into the feeding trough and falls onto the chilling roll, forming a thin somewhat translucent film which quickly cools and solidifies. The solid fat is removed by a scraper and falls into a picker trough. The latter contains a shaft equipped with beating and conveying blades which churn the composition and destroy the translucency, producing an opaque white product of lard-like appearance. The picker is run at a relatively high speed, say 175 to 180 r.p.m. Figure 91 is an end view showing chill roll, feeding trough and picker. In Fig. 93 the cooler and picker appear on the left hand and in the center is a pump which withdraws the product from the picker and forces it through the pipe line to the packaging cocks on the right hand.

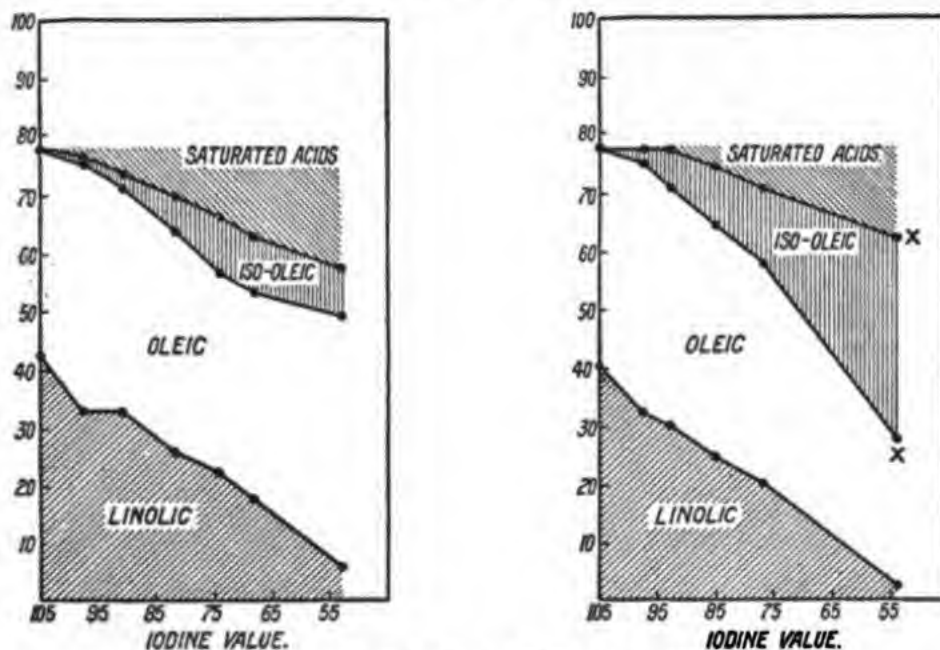


FIG. 90.—SEE PARA. 3773, PAGE 429.

Cottonseed oil hydrogenated by the drip method.

Ratio: Oleic : iso-oleic :: 10 : 1.8

Cottonseed oil hydrogenated by the over-flow method.

Ratio: Oleic : iso-oleic :: 10 : 14.5

Too high a speed of the picker blades incorporates an excessive amount of air in the product rendering it "fluffy."²

3905. The speed of rotation of the chilling roll is governed by the rate of feed and by the temperature of the brine. The latter may be kept between, for example, - 5° to + 10° F. for good results. If the brine is too cold, the product is liable to drop badly from the roll and the texture is not always satisfactory. This, however, may be largely remedied by increasing the feed. In winter the brine may be held at a slightly higher temperature to prevent brittleness. In the hottest weather, very cold brine should be used to aid in securing a product which will preserve its color and consistency for a considerable time.

² The author desires to make acknowledgment to the Albright-Nell Co. of Chicago for their courtesy in furnishing the illustrations Figs. 91-92 and 93a.

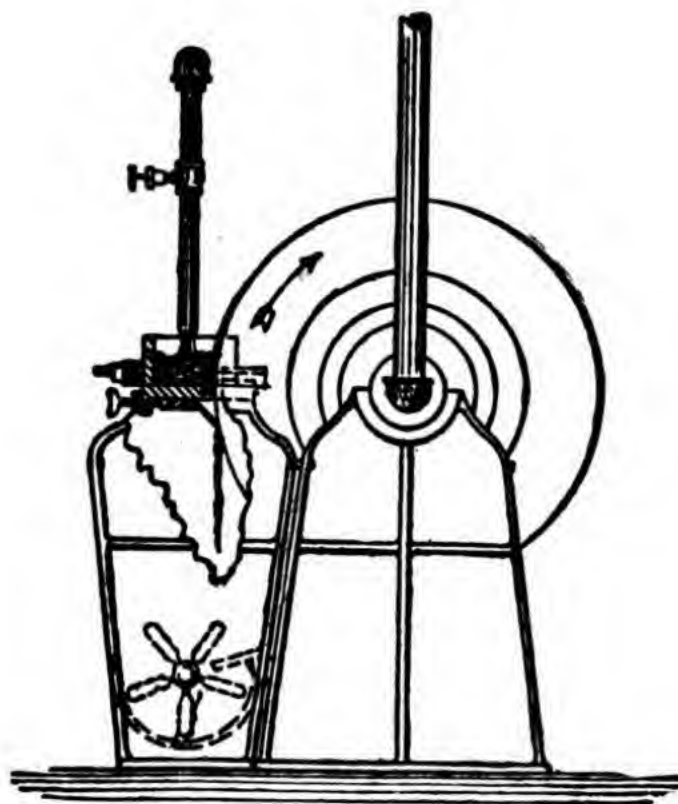


FIG. 91.

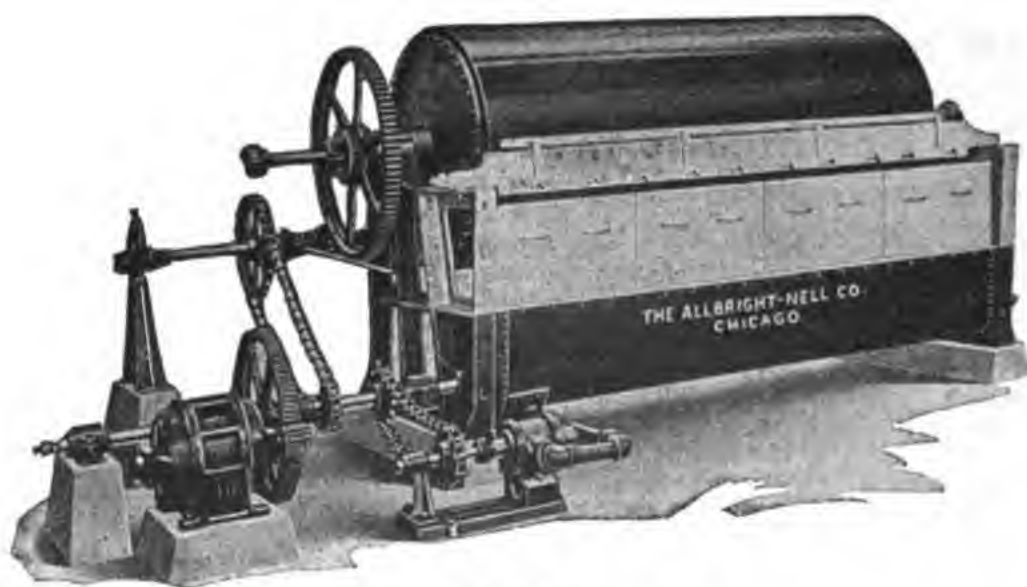


FIG. 92.

3906. When properly made the compound containing the hydrogenated oil thickener is excellent in color, texture, flavor and keeping qualities. By many it is considered superior in several respects to oleo-stearin compound.

3907. Possibly, however, for best results as to stability it is desirable to hydrogenate the entire body of oil to a fatty acid titer of 36 or 38, or whatever consistency may be required, rather than to take a relatively small proportion of the oil and harden it to a titer of 50 to 60 or thereabouts and incorporate with unhydrogenated oil. It appears that the hydrogenation of the total body of the oil, by transforming the linoleic and linolenic compounds and the like, has a tendency to improve the oil as regards its edibility and certainly gives it greater stability. The flavor of lard compound is, however, preferred by many large users of lard substitute presumably because of the proportion of normal oil which it contains, and the manufacturing cost is lower.

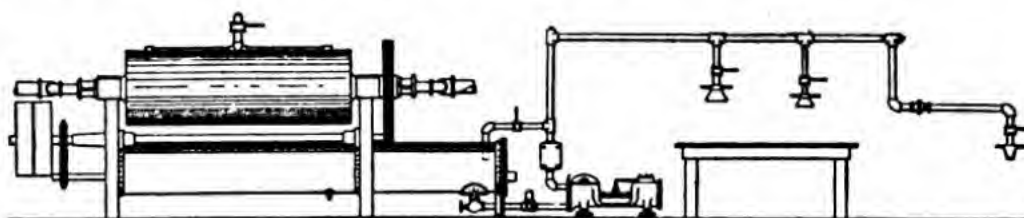


FIG. 93.

3908. Further, it may be stated, by partial saturation of glycerides, we have the possibility of preparing from tri-olein the oleo-distearin or the dioleo-stearin. Dioleopalmitin would give either oleostearopalmitin or distearopalmitin. From tri-olein we may have the two isomeric oleo-distearins, α - and β -oleo-distearin as well as α - and β -dioleo-stearin. Which of these we may be able to produce controllably and which may prove best from the edible standpoint are problems for the future to solve.

3909. Joslin calls attention to the economy in using hardened oil "vegetable stearin" in place of oleo-stearin for making lard compound, since only 7 to 10 per cent of the former is called for against 14 to 20 per cent of the oleo-stearin. Of course the amount of hardened oil required depends on its degree of "hardness," but for the present grades of hydrogenated cottonseed oil of 58 to 60 titer, now on the market, the above proportions hold. When the oil is hardened to about the consistency of average oleo-stearin, naturally a greater proportion is needed in lard compound.

3910. Joslin notes the economy resulting from the employment of hardened oil at one plant during a period of one year.

93 parts cottonseed oil at \$6.45 per hundred pounds.....	\$6.00
7 parts hardened oil (vegetable stearin) at \$9.25 per hundred pounds...	0.65

Cost per hundred pounds of compound.....	\$6.65
86 parts cottonseed oil at \$6.45 per hundred pounds.....	\$5.55
14 parts oleo-stearin at \$9.25 per hundred pounds.....	1.29

Cost per hundred pounds of compound.....	\$6.84
--	--------

Or a saving of practically 20 cents per hundred pounds of compound manufactured on the basis of prices then prevailing. This differential, of course, will change with altered price conditions.

3911. Brauer ³ notes that both laboratory experiments and those made on a commercial scale indicate that hardened fats have a much greater capacity for "holding" water than untreated fats, and that the same is true of margarines made from the two kinds of fats. Margarines made of (a) hardened whale oil and unhardened linseed oil, (b) hardened linseed oil mixed with unhardened oil, and (c) tallow and unhardened linseed oil, contained 25.67 per cent, 18.33 per cent and 11.75 per cent, respectively, of moisture.

3912. The fat-soluble accessory growth substances of beef fat and "oleo-oil" are considered important food elements by Halliburton and Drummond.⁴ Margarines containing these bodies are nutritively equivalent to butter. On the

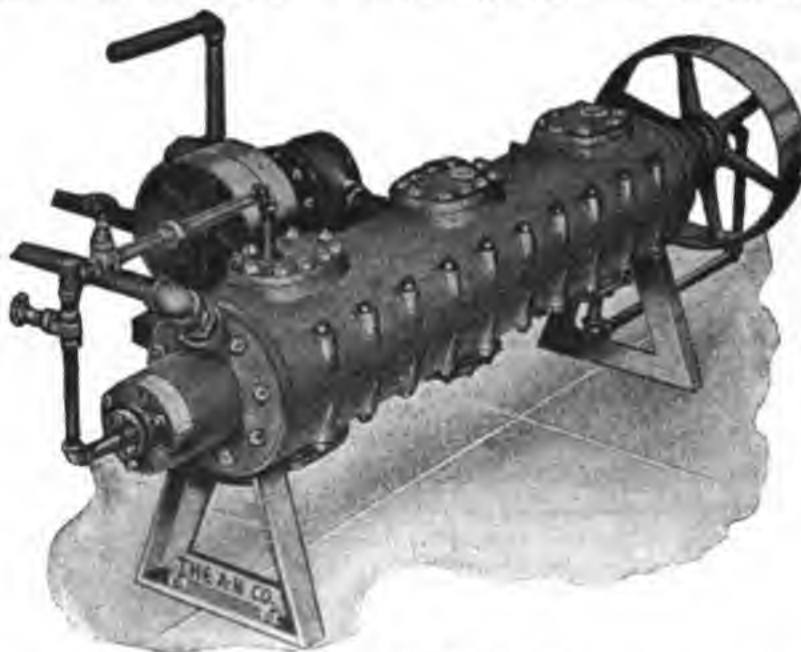


FIG. 93a.—LARD BLENDER.

Lard compound is further improved by passing through a blender, after leaving the chill roll.

other hand it is asserted that cocoanut oil, cottonseed oil, peanut oil and hydrogenated vegetable oils contain little of these accessory substances and that margarines prepared from these are not equal to butter in nutritive value. A commercial butter substitute prepared from cocoanut oil and skimmed milk is said to contain the full proportion of Vitamin A.

3913. Clayton ⁵ observes that excessive moisture content of margarines from hydrogenated oil has not been met with in British factories.

3914. The utility of hydrogenated oils in the manufacture of oleomargarine receives further confirmation by Pickard,⁶ who states that for the purpose hydro-

³ *Z. öffent. Chem.*, **22**, 209; *Chem. Zentr.*, 1916, II, 527; *Chem. Abst.*, 1917, 1699; *Z. angew. Chem.*, 1916, **29**, Ref., 492; *J.S.C.I.*, **1917**, 98.

⁴ *Journal of Physiology*, 1917, **51**, 235-251. *J. Chem. Soc.*, 1917, **112**, i, 673. *J.S.C.I.*, **1917**, 1285; cf. Dannemeyer, *Volksernährung*, **2**, 193; *Chem. Ztr.*, **1927**, II, 1219.

⁵ *J.S.C.I.*, **1917**, 1205.

⁶ *Am. Food J.*, **1918**, 16.

genated or hardened oils are used in considerable quantities. He further states that when the process is properly handled, the melting-point of the resulting material can be regulated to a nicety and the oils contain no appreciable amounts of deleterious substances, so that they are, therefore, perfectly wholesome and, in consequence, legitimate constituents of edible products.

3915. Keebler states that the principal difficulty experienced with some manufacturers of nut margarine is that of keeping the melting-point above 75° F., while butter melts about 92° F. However, it is claimed by one manufacturer that his nut margarine has a melting-point of 107° F. Keebler observes that this possibly can be accounted for by the use of hydrogenated oils.

3916. Butter Substitute from Peanuts. Sherman ⁷ prepares a butter substitute by mixing hydrogenated peanut oil with a "milk powder" substance obtained by leaching the fat-free meat of the nuts and evaporating the liquid.

3917. Burchanal ⁸ prepares a food compound closely simulating lard in its physical and chemical characteristics, consisting of a mixture of an oil and a hardening agent produced by hydrogenizing an oil or liquid fat.

In its most desirable form, the product is a vegetable one, consisting of a mixture of about 85 per cent of cottonseed oil and 15 per cent of hydrogenized cottonseed oil. In the manufacture of this product, oil is hydrogenized, by vigorous agitation in a closed vessel containing an atmosphere of compressed hydrogen, a catalytic agent, such as kieselguhr impregnated with finely divided nickel, being maintained in suspension in the oil and the charge being heated to a temperature of about 155° C. The oil is thereby converted into a white or yellowish solid, containing additional hydrogen about .5 to .6 per cent more than in the non-hydrogenized material, having a saponification value of about 190, an iodine value of about 20, a melting-point of about 56° C., and a titer of about 55° C., giving no reaction for cottonseed oil under the Halphen test. Suitable proportions of the hydrogenized oil are now thoroughly mixed or blended. In case about 15 per cent of hydrogenized cottonseed oil and 85 per cent of non-hydrogenized cottonseed oil are thus mixed, the final product is stated to be a white or yellowish semi-solid, having a saponification value of about 195; an iodine value of about 95; a melting-point of about 42° C.; and a titer of about 36° C.

In case a harder hydrogenized stock is used, its proportion may be correspondingly reduced. For example, if the oil used for hardening is hydrogenized to an iodine value of 8 or 9, approximately 10 per cent of the hardened material are stated to be required to yield a mixture having physical constants approximately as above specified.

3918. Burchanal ⁹ produces an incompletely hydrogenated lard-like fat from cottonseed oil, with the stated object of providing a new food for a shortening in cooking, in which the liability to become rancid is minimized, and in which the components of such vegetable oils which are inferior and detrimental to use as such a food product have been, to a large extent, converted into a higher and more wholesome form.

3919. All such vegetable oils contain glycerides of unsaturated fatty acids, and among these, notable quantities of fatty glycerides of lower saturation than olein. Oxidation is largely the cause of rancidity, which oxidation weakens the fat at the point of absorption at the double bonds, and these glycerides of lesser saturation readily absorb oxygen from the air at ordinary temperatures, while the more highly saturated glycerides, as olein, only absorb oxygen at elevated temperatures. It is evident, Burchanal observes, that oils or fats containing notable quantities of glycerides of linolic acid, or of lesser saturation, are distinctly

⁷ U. S. Pat. 1,691,087, Nov. 13, 1928, assigned to Brown Co.

⁸ U. S. Pat. 1,135,935, Apr. 13, 1915.

⁹ U. S. Pat. 1,135,351, Apr. 13, 1915. This is the patent which was involved in *The Procter & Gamble Company vs. Berlin Mills Company*.

inferior as an edible product to those containing a minimum of these glycerides with a larger per cent of olein. On the other hand, while it is important to get rid of the readily oxidizable glycerides of lower saturation it is also important not to supply too large a per cent of fully saturated glycerides. The saturated glycerides of the arachidic, stearic, palmitic and other groups are stated to be of very small value for shortening, inasmuch as it is the liquid fats which contribute this value to the material. Saturated fats, however, serve the purpose of congealing the shortening within the food, and thus retain it equally distributed throughout the whole. Oil, liquid at the ordinary temperatures, is not regarded as making the best shortening, because the oil remains liquid, keeping the food in a soggy condition, and the oil will even settle to the under part of the cooked product. Moreover, fats of a melting-point above the temperature of the human body, 98° F., are not so digestible as fats which are liquid at this point, or which have a melting-point below 98° F. Burchanal therefore endeavors to change the chemical composition of the oil (cottonseed) to obtain a product with a high percentage of olein, a low percentage of linolin and the lesser saturated fats, and with only sufficient stearin to make the product congeal at ordinary temperatures.

3920. Hydrogenation is, therefore, stopped when the oil has been converted into a product which cools to a white or yellowish semi-solid resembling lard. In many respects, it is claimed the product is superior to the best leaf lard as a shortening. It is not so liable to become rancid and the product can be heated to a considerably higher temperature than lard without smoking or burning. The high temperature to which the product can be raised without smoking or burning is stated to make the product ideal for frying as a crust forms almost instantly on the food fried, which prevents any absorption of the shortening. Burchanal gives data on the analytical constants of the product. A lard-like product thus prepared from cottonseed oil has a saponification value of about 195; and an iodine value ranging from about 55 to about 80. The product having an iodine number of 55 has a titer of about 42° and a melting-point of about 40° C.; that having an iodine value of 80 has a titer of about 35° and a melting-point of about 33° C. While but partially hydrogenized, containing from about 1.5 per cent to 2.5 per cent of additional hydrogen more than in the non-hydrogenized material, it shows no free cottonseed oil when subjected to the Halphen test. It contains from 20 to 25 per cent of the fully saturated glycerides, from 5 to 10 per cent linolin and from 65 to 75 per cent olein, and an average of a number of samples gives 23 per cent of saturated fats, 7.5 per cent linolin and 69.5 per cent olein, while the cottonseed oil before treatment contained 37 per cent linolin and 46 per cent olein.

3921. Walker¹⁰ proposes a method of making fatty food products which consists in partially hydrogenating unsaturated compounds of vegetable or animal oils and fats by any method and arresting the operation at a predetermined point short of saturation and, where the consistency of the product is above or below that of a given oil or fatty body, and then incorporating with the partially hydrogenated body an unhydrogenated oil or fatty body to produce a product of the desired consistency and having the characteristic flavor desired. For example, purified cottonseed oil is hydrogenated until the action reaches a point where the stearin produced amounts to about 22 per cent of the oil treated, there remaining about 80 per cent of unsaturated oil. These proportions may vary with wide limits, depending on the consistency of the final product desired and the nature of the subsequent additions. To the hydrogenated product freed from catalyzer, oily lard is added, preferably by means of incorporating rolls, the quantity being sufficient to give to the hydrogenated product a lard consistency.

3922. The process is stated to be equally applicable to making butter substitutes, the manufacture of coatings for chocolate creams, confections and the like.

¹⁰ U. S. Pat. 1,206,954, Dec. 5, 1916.

3923. Walker considers it is important that the hydrogenating action be carried to a point affording a consistency above or below that of the final product, and then to secure the desired consistency by incorporation of a suitable oil or solid fatty body, thereby securing the benefits of the added body as a hardening or softening agent while retaining its desirable flavoring characteristics unimpaired. In general, the hydrogenating action may vary between a product which is soft and greasy to a solid, but for the preparation of lard and butter substitutes the hydrogenating action should afford a product containing about 18 to 22 per cent of stearin.

3924. An edible oil composition is described by Ellis ¹¹ comprising hydrogenated cottonseed oil and cocoanut oil, the mixture being beaten with air to improve the color of the product. The following formula and method of treatment are given: 90 parts cottonseed oil are mixed with 10 parts of cocoanut oil and the mixture subjected to the action of hydrogen at a temperature of from 150° to 160° C., in the presence of finely divided nickel so as to convert a proportion of the unsaturated into saturated material. A soft solid composition is produced which is then subjected to aeration carried out by beating the hydrogenated product with rapidly revolving paddles until a sufficient quantity of air is incorporated in the product, in a finely vesiculated condition to produce a material of the proper consistency and light-colored appearance. Another statement ¹² gives details of a hydrogenated butter substitute in which various hydrogenated and normal oils are incorporated to make a fat approximating the melting-point of butter, with which is mixed milk, etc., to produce a variety of margarine. These compositions should ordinarily have a melting-point considerably less than the temperature of the human body, so that when the material is taken into the mouth, it immediately melts and does not leave an unpleasant greasy sensation on the tongue and walls of the mouth. It is generally desirable to carry the hydrogenation treatment to a point where a product of rather firm consistency is secured. This produces a material, however, which is of too high a melting-point for the production of a vegetable butter composition. Hence it is then pressed to remove the excessive amount of stearine. In the case of cottonseed oil, it is stated that it is desirable to hydrogenate until the iodine number falls to about 80. The oil may then be cooled to about 30° C., and allowed to stand for a time and pressed. Afterwards it is warmed to render it entirely fluid, and is incorporated with ordinary full milk or skim milk or buttermilk, sterilized milk, sour milk or milk which has been specially fermented. Coloring material, such as ordinary butter color, may be added. Also a flavoring compound, such as cumarin and various esters and aldehydes, such as those of valerian and capryl bodies, may be added. In order to give the product the property of browning, when heated in a skillet, bodies such as egg yolk, milk sugar, lecithin or finely powdered casein may be introduced.

3925. A suitable oil base having been derived in this manner, the oily material is emulsified with the milk. For 100 parts of fatty material about 30 to 60 parts of full milk or perhaps 50 to 80 parts of skim milk are suitable proportions. In the summer months a stiffer composition is required than in the winter months and the fatty material should be compounded to give a material melting at the proper point with reference to seasonal temperatures. In emulsifying it is desirable to put a portion of the milk in the beating apparatus, and to stir for a short time. In the case of full milk, beating for ten minutes or so causes a separation of the butter fat. The oil then may be added in portions, beating thoroughly until the composition is well incorporated. The remainder of the milk and fatty material may be added from time to time, and the temperature of the mixture should preferably be maintained between 30° and 40° C. When thoroughly incorporated, the batch is run from the apparatus into a cooling device which cools the emulsified composition rapidly. It is then ready to be rolled and kneaded to remove the excess of water, after which treatment the material is formed into the desired shape for shipment. The coloring material and salt and also flavoring material may be added during the emulsification process ¹³

¹¹ U. S. Pat. 1,037,881, Sept. 10, 1912.

¹² Ellis, U. S. Patent, 1,038,547, Sept. 17, 1912.

¹³ The use of hardened oil in preparing oleomargarine compositions is the basis of French Pat. 458,611, of 1913, to Deveau.

3926. Hydrogenated soya-bean oil¹⁴ has been recommended, as well as hydrogenated vegetable oil and animal fats mixed to form lard-like products of varying composition. When employing cocoanut oil in such compositions it is desirable to hydrogenate it. To be sure, cocoanut oil usually has an iodine value of only 7 to 10, which is indicative of the small proportion of unsaturated bodies present. But, in spite of this, in order to secure a permanent product, which does not separate or grow lumpy on standing, and which remains in a perfectly neutral condition for a long period of time, even when exposed to the air, it is desirable that the iodine number of the cocoanut oil should be reduced practically to zero, if larger proportions than 30 per cent or thereabout are incorporated with hydrogenated soya-bean or cottonseed oil. Cocoanut oil may be pressed to separate stearin from olein and the latter hydrogenated.

3927. An edible product of a so-called superhydrogenated character¹⁵ is obtained by carrying the degree of hydrogenation beyond the actual titer required and then pressing to remove some of the harder material so that the final titer of the expressed fat is that of lard, butter or whatever other titer may be required. Most oils of a vegetable nature and some animal oils contain from traces up to considerable quantities of highly unsaturated bodies, including those of the linoleic and linolenic group. These and other similar bodies are very sensitive to oxidation and lend instability to edible oil products of this character by their tendency to change chemically and thus alter the flavor of the material. These bodies may be saturated by very careful hydrogenation up to the degree of consistency required in the edible product, but such hydrogenation is difficult to carry out commercially on a large scale with the assurance that the product will run uniform in quality. By saturating with hydrogen to an excessive degree as regards final consistency, these bodies become more completely divested of odor of origin and tendency to rancidify. By hydrogenating cottonseed or corn oil or similar oils to reduce the iodine number materially, the more sensitive double bonds are saturated with hydrogen and oxidation tendency is reduced. Apparently the complete elimination of all the double bonds characteristic of the linoleic type is more difficult than the removal of the double bonds characteristic of the linolenic type, so that control over this seeming selective action during hydrogenation when saturating up to a given degree of consistency from a given oil is difficult, if not impossible, under ordinary conditions of hydrogenating. If, however, the oil is overhydrogenated so that a more consistent fat is acquired than is actually desired for an edible product, the unstable bodies thus may be completely transformed. In order to secure the degree of consistency desired the hot hydrogenated fat is gradually cooled to about 30° C., when the temperature may be maintained between 25° to 35° C., or so for several hours to induce crystallization or balling of the high melting-point compounds. The mass is then pressed.

3928. It has been noted when a vegetable oil such as cottonseed oil is hydrogenated directly until of the consistency desired that on cooling frequently it tends to granulate unless rapidly cooled. This is objectionable in culinary operations as an initial lard-like body after once heating and slow cooling in the air often forms relatively hard granules of stearin-like bodies which look like little balls of coagulated material and separating as they do from the fluid oil under some circumstances give the product the appearance of having curdled or decomposed. By superhydrogenating and pressing to the point required the granulating stearins or stearin-like bodies are eliminated to a greater or less extent and less easily crystallizing or non-granulating stiffening bodies remain tending from their amorphous texture to maintain better the original consistency and appearance of the product in repeated culinary use.

3929. The Boyce process¹⁶ of producing an edible compound consists in preparing a mixture of synthetic stearin by the action of hydrogen in the presence of a catalyzer upon a previously unsaturated oil or fat, the latter being subjected to the catalytic action of hydrogen to a degree sufficient to convert the required fraction of the oil into synthetic stearin. The hydrogenation process is arrested at the point when the stearin is found to be present in the amount of about 20 per cent of the entire body of the oil. Boyce states that by arresting the action at this point there will remain a mixture of the unsaturated oil and the synthetic stearin produced by the hydrogenation of a portion of the oil.

3930. A hydrogenated fatty food product containing hydrogenated corn oil has been described.¹⁷ When corn oil is suitably by hydrogenated, a product is derived which has the

¹⁴ Ellis, U. S. Pat. 1,047,013, Dec. 10, 1912.

¹⁵ Ellis, U. S. Pat. 1,058,738, Apr. 15, 1913.

¹⁶ Boyce, U. S. Pat. 1,061,254, May 6, 1913, assigned to the American Cotton Oil Co.

¹⁷ Ellis, U. S. Pat. 1,067,978, July 22, 1913.

property of improving the stability of hydrogenated cottonseed oil or similar hydrogenated oils which tend to granulate. Also it is stated that hydrogenated cocoanut oil may be used as a fluxing agent for chocolate in the manufacture of confectionery. The melting-point of the fatty flux should preferably be about 90° to 100° F. Hydrogenated cocoanut oil olein may be used in a similar manner. The manufacture of the coating of chocolate creams calls for a relatively high melting-point fat which incorporates readily with chocolate and does not impair its flavor. Cocoa butter is especially desired on this account, but is relatively expensive. Cocoanut oil melts so easily that in hot weather candies made with it soften very quickly when handled. Cocoanut oil also has a tendency to rancidify. By hydrogenation of an oil assimilable with chocolate the exact melting-point desired may be obtained and a stable composition secured.¹⁸

3931. Hydrogenated oil of high titer may be mixed with unhydrogenated oil to form a body of a consistency suitable for use as a substitute for lard. For example, hydrogenated cotton oil of a titer of say 52° C. (fatty acids) may be melted and incorporated with four times its weight or so of ordinary refined or deodorized cottonseed oil so as to form on cooling a white, opaque fatty material of the consistency of ordinary lard. The product made in this manner is not always sufficiently color-stable. Not infrequently in a short time it will lose its opacity to a considerable degree and will take on an appearance more suggestive of petrolatum than lard. Sometimes this change, which may be due to a tendency to form solid solutions of certain types, occurs irregularly in layers of isolated zones which give the product a curious mottled appearance, and this striated effect taking place in the containers during storage so changes the product, physically at least, that it is regarded as damaged or unfit for use by those accustomed to the normal appearance of lard. By disseminating through a fatty basis of a melting-point and consistency approaching that of lard, a quantity of fatty material of higher titer so as to form flocculations of a high titer product uniformly disseminated through the fatty basis, a product of better "color stability" is secured.¹⁹ The material of the relatively higher titer may be denominated the stabilizer and the proportions of fatty basis and stabilizer as well as their melting-points and titers may be varied to meet various conditions of a climatic nature.

3932. As an illustration one may take to make the fatty basis, 6 parts of hydrogenated cottonseed oil of a titer ranging between 52° to 54° C. (fatty acids) and 34 parts of refined and deodorized cottonseed oil. A thorough mixture is secured by the aid of heat and when well incorporated the melted product is chilled rapidly in a thin layer by feeding onto a chilled roll which is kept in constant rotation and from which the solidified product is removed in layers by a scraper. This product when properly set has a consistency approaching that of ordinary lard. The stabilizer is prepared by incorporating 3 parts of hydrogenated cottonseed oil of the same titer as that used in making the fatty basis, with 5 parts of refined and deodorized cottonseed oil. By heating the hardened oil with the deodorized oil the requisite mixture is obtained. As in making the fatty basis, the stabilizer is likewise chilled to form a solid, and the two products are mixed in powerful mixing apparatus. To secure a desirable distribution both the fatty basis and the stabilizer may be fed onto the same chill roll in a series of adjacent or alternate streams, or the fatty basis may be allowed to fall on the chill roll, and when it has progressed a distance sufficient to solidify but not to stiffen it fully, the stabilizer is applied as a superposed coating adherent to and slightly intermingled at the contacting surfaces, with the fatty basis. This composite film is removed by the scraper and is then "pugged"

¹⁸ Cf. Whympers and Bradley, *J.S.C.I.*, 1925, 44, 77T on advantages obtained by use of hydrogenated oil in chocolate coatings to prevent "fat bloom."

¹⁹ Ellis, U. S. Pat. 1,070,331, Aug. 12, 1913.

or beaten. As the melting-point of the stabilizer is preferably considerably higher than that of the fatty basis, the former congeals more quickly, so that although the superposed film is somewhat insulated from the chill roll by the fatty basis film yet the solidification of the upper layer is usually rapid enough to prevent material solution or interfusion of the two heterogeneous layers.

3933. Further modifications are the following: 80 parts of cottonseed oil are mixed with 15 parts of hydrogenated oil of a titer of 48 (fatty acids). This is chilled and mixed with 5 parts of melted 42° C. titer hydrogenated or hard oil, or fat. Likewise one can superpose on a basis of 34 to 38 titer about 20 per cent of 40 to 42 titer. Cottonseed oil may be hydrogenated to 37 titer, chilled as described and similarly incorporated with about 10 to 20 per cent cottonseed oil hydrogenated to 40 to 42 titer. Thus there may be obtained a lard-like or otherwise consistent fatty material having its main titer to a considerable degree influenced so that the product may have the desired soft consistency of ordinary lard while actually containing bodies which if melted into the fatty basis would raise the melting-point and consistency.

3934. Palm oil, suitably hydrogenated, has been recommended for use in edible fat products.²⁰

3935. A product called Vegetole, manufactured by Armour & Co., according to the *American Food Journal*, June, 1917, page 330, is a hydrogenated cottonseed oil, without flavor and fully sterilized. It is stated that Vegetole differs slightly from lard and also mixtures of cottonseed oil and oleo-stearin and that it also has different properties from cottonseed oil. Vegetole is sweet, wholesome and nutritious and easily digested and can be used for all purposes for which lard is used. As a shortening agent, whether in bread, pie crust, or biscuits, or when used as a medium for frying, the results obtained are stated to be excellent.

3936. A liquid hydrogenated oil food product is described by Lowenstein which is stated to be suitable for use as a salad oil, cooking oil or for such other purposes as cottonseed oil, or similar oils have been used, the product being superior to such oils in keeping qualities. See para. 3268, page 333.

3937. A further advantage of the product lies in the fact that the dissolved stearin therein is found to crystallize most readily, which quality renders the product especially suitable for winter or cold pressing for salad oil.

3938. In carrying out the process for the manufacture of the product, a fatty oil, for instance, choice or prime yellow cottonseed oil, is placed in a closed vessel and caused to be chemically combined with hydrogen in the presence of a catalyzer. A temperature of 150° to 200° C. has been satisfactorily employed and the time required to produce the desired result after attaining this temperature is from five to thirty minutes, depending upon the activity and proportion of the catalyzer employed.

3939. Depending upon the particular cottonseed oil treated by the process the iodine value of the finished product varies from about 90 to 102. Its titer (as determined by the Wolfbauer method) has been slightly increased during the process to the extent of from about 1° C. to 1½° C. over that of the original oil treated. The color of the treated product is usually somewhat lighter than the original oil. On cooling the product it in part readily crystallizes, thereby making the separation of stearin from the oil much easier and more effective for "winter pressing" for salad oil than is the case with ordinary cottonseed oil. The product responds negatively to the Milliau test for cottonseed oil.

3940. Improvement in Edibility of Vegetable Fats by Partial Hydrogenation.²¹ Edible vegetable fats are hydrogenated in carefully regulated stages—at 70° C. to decompose aldehydes and ketones and then under 250–600-lb. pressure at 90° to decompose hydroxy-fats—without hardening the fat.

²⁰ Ellis, U. S. Pat. 1,087,161, Feb. 17, 1914.

The fatty acids of Kaya oil have been hydrogenated by Ueno (*Chem. Rev. u. d. Fell. u. Harz. Ind.*, 1913, 209) who thereby obtained fatty acids melting at 65.5° C.

²¹ U. S. Pat. 1,605,108 to Grindrod (assignor to Carnation Milk Products Co.).

3941. Partial Hydrogenation of Oil for a Food Product. A liquid product of improved quality is obtained from a vegetable oil by subjecting the oil to hydrogenation, stopping the hydrogenation at a point at which the oil solidifies at 21°-27°, and then separating the liquid from the solid constituent. The liquid food product so obtained has an iodine value of about 90 and remains clear for at least five hours at 0°. ²²

3942. Qualities Sought by Bakers in a Hydrogenated Oil. Aspergren, writing in *The Cotton Oil Press*, November, 1927, says that to the cracker baker a low melting-point and not more than a small amount of highly unsaturated glycerides are desiderata, while the cake baker, using hydrogenated oil, wishes for one which has high water-absorption qualities and which will cream well.

3943. Graff ²³ writing of vegetable oils as shortening, says that hydrogenation has greatly improved this class of shortening. In the first place the reduction of readily oxidizable oils such as the glycerides of linoleic acid has made these oils more stable and has diminished or abolished the tendency to rancidity. This is of special importance to the cracker (*anglice* biscuit) baker because his merchandise has to be kept so long before it is consumed. In the second place, hydrogenation furnishes a complete range of consistencies from hard waxy fats to buttery semi-solids.

3944. In the manufacture of leavened bread it is the practice to add various milk products to improve the flavor, etc. The addition of milk tends to retard fermentation by yeast and Kohmann, Godfrey and Ashe ²⁴ have found that by peptonizing the milk the fermentation is accelerated rather than retarded.

3945. In addition to milk they find that various forms of cheese may be employed and that it is preferable to mix the cheese with a hydrogenated fat such as hydrogenated cottonseed oil having a melting-point of about 35° to 40° C. A creamy mixture is obtained by incorporating these ingredients and such mixture may be readily introduced into the dough batch during the usual mixing operation. The addition of the hardened fat to the cheese is desirable for the further reason that the fat replaces a part or all of the shortening agents that are ordinarily added to bread. Ten parts of cheese to 4 or 5 parts of the hardened fat may be employed and 1 to 1½ lb. of this mixture may be used to 100 lb. of flour.

3946. Kohman, Godfrey and Ashe employ hydrogenated fats in the manufacture of bread. ²⁵ A shortening effect equal in value to that produced by relatively large quantities of liquid oil is stated to be obtained by the employment of a hard fat, which also permits the use of sufficient water not only to supply the amount required for giving stiffness and springiness to the dough, but to supply, in the baked loaf, the quantity recognized as desirable for imparting to the bread the expected freshness and flavor. The employment of the hard fat as the shortening agent is likewise found to add to the keeping qualities of the loaf, in the sense that even after the loaf has lost its original freshness, it lacks the rancidity frequently met with in ordinary bread which has been kept, under the same conditions, for the same period of time. For the present purpose they use as the shortening agent, a hard fat of either vegetable or animal origin,—as, for instance, hydrogenated edible vegetable oil (hydrogenated cottonseed oil), hydrogenated edible animal oil, or oleo-stearin. Kohman, Godfrey and Ashe give preference to the use of hydrogenated cottonseed oil, or other hydrogenated vegetable oil of an edible character, for the stated reason that such oils are relatively cheap, and can be hydrogenated or hardened up to a high melting-point readily and conveniently. Thus hardened cottonseed oil having a melting-point of 57° C. is well adapted for shortening purposes.

²² U. S. Pat. 1,483,155, Feb. 12, 1924; original application June 1, 1914, renewed June 22, 1923, to Boyce (assignor to The American Cotton Oil Co.).

²³ *Ind. Eng. Chem.*, 1928, **20**, 1310.

²⁴ U. S. Pat. 1,222,304, Apr. 10, 1917.

²⁵ U. S. Pats. 1,204,280 and 1,204,281, Nov. 7, 1916.

3947. To incorporate the hard fat of high melting-point into the dough batch it is desirable to bring the former first into intimate admixture with flour. This may be effected by melting the hard fat and heating it somewhat above its melting-temperature and then mixing the flour therewith. The heating and mixing operation may be carried out in a rotary drum, having a heating jacket, and provided with stirrers. The temperature should be maintained, during the mixing operation, above the melting-point of the fat, so that the flour shall not chill the mass, or the flour may be preheated, for the same purpose. It is found that under these conditions a quantity of flour equal in weight to from 5 to 10 times the weight of the melted fat will absorb the fat, and that the flour will retain its pulverulent condition. The procedure involves heating only a relatively small quantity of the flour. Thus, if 1 lb. of hard fat is to be added to a dough batch containing 880 lb. of flour, it will suffice to absorb the fat in 5 to 10 lb. of flour, in the manner described, and it is found that in the subsequent mixing and kneading of the dough batch, the shortening thus added to the relatively small amount of flour will be uniformly distributed throughout the entire mass. This feature avoids heating the entire mass of flour up to the temperature of the small portion which has absorbed the fat.

3948. The hard fat may also be incorporated with the flour in the manner following: The melted fat heated to a temperature of 200° C. and upward may be supplied from a suitable melting and heating receptacle to a discharge pipe from which it may be ejected, at a correspondingly high temperature, in the form of a fine spray or cloud, by a jet of air into an inclosed chamber. Into this chamber the flour may be sifted, and on coming in contact with the highly heated particles of fat sprayed into the chamber, take up the fat. The flour thus impregnated with the melted fat remains in a pulverulent condition, after cooling, and is available for use as a part of the flour ingredient of the dough batch. In this case it is found that by repeating the absorbing operation a number of times, upon the same body of flour a quantity of flour from five to ten times the weight of the fat is sufficient to absorb the fat and yet remain in a pulverulent condition.

3949. It is found that, with equally good results as to color, texture and expansion, a quantity of the melted fat incorporated with the flour in either of the ways described may be employed of approximately one-twentieth the weight of the cottonseed oil used ordinarily in making up the dough batch. Thus, in those instances where from 2 to 3 per cent of cottonseed oil (calculated, by weight, on the amount of flour employed in the dough batch) was used, one-twentieth of that percentage, by weight, of hydrogenized cottonseed oil having a melting-point of 57° C. may be used, resulting, it is claimed, in like shortening effects with the production of a stiffer and springier dough; the viscosity of the dough being maintained, even though the absorption is increased, and the resultant baked loaf having an amount of moisture sufficient to give it satisfactory freshness and flavor.

3950. Fats of a melting-point as low as about 35° C. can be used and the advantages incident to the use of the hard fats secured, although to a somewhat lesser degree than when the shortening agent consists of the higher melting fat without appreciable admixture of liquid fat. Even when fats of a melting-point as low as 35° C. are employed, the amount of the shortening agent in proportion to the flour of the bread is but a fraction of the amount of liquid shortening agent required for producing the same shortening effect and need not exceed 5 lb. of fat to 880 lb. of flour and bread. Fats of higher melting-point require a correspondingly less proportion by weight of fat to flour to produce the same shortening effect, and, when the melting-point of the fat approximates 57° C. the amount of the fat may be diminished to say 2 lb. of fat to 880 lb. of flour of the bread. In fact, the higher the melting-point of the fat, the less quantity, in proportion to the flour employed, will be required to obtain a baked loaf of satisfactory shortness, moisture-content and keeping qualities.

3951. In a modification of the process of making a shortening composition ²⁶ Kohman, Godfrey and Ashe heat flour to 200° C. or higher and atomize hydrogenated oil by means of a jet of air into the flour. To secure this admixture, the flour is sifted in at the top of a chamber into which the atomized oil is being introduced and on coming in contact with the colder particles of flour the hydrogenated fat is taken up by the flour. The latter remains in pulverulent condition after cooling. By repeating this absorbing operation a number of times

²⁶ U. S. Pats. 1,242,883, and 1,242,884, Oct. 9, 1917.

upon the same body of flour, the latter will take up from one-tenth to one-fifth of its weight of the fatty material and yet remain in a pulverulent condition. As shortening material, this powder may be admixed with the requisite amount of flour and other materials used in making bread, thus introducing the shortening in a simple manner.

3952. Hydrogenated oil in the form of a powder is suggested by Atkinson ²⁷ as a shortener. Corn oil is hardened to a melting-point of about 148° F., and is ground in a mill having cooled rolls to give a fine powder. During the pulverization the temperature of the fat should be kept below its melting-point. The powder is stated to be particularly useful as a shortening composition for cereal baking products as it may be added to the flour or dough in definite quantities in lieu of lard, butter, or other solid or liquid shortening material and is more easily mixed with flour and dough than ordinary shortening fat or oil.

3953. An edible product containing hydrogenated oil and carbohydrates in the form of a powder or as a solid cake is described by Ellis.²⁸

3954. A shortening and leavening composition employing hydrogenated oil is suggested by Holbrook,²⁹ who finds it possible to incorporate the components of baking powder with thickened cottonseed oil to produce a composition which is stated to be stable and which, when mixed with flour and water to form dough, will serve both to shorten and leaven the mass.

3955. The cottonseed oil is thickened to the desired consistency in any suitable manner, but, preferably, by partial hydrogenation or by mixing it with from 6 to 10 per cent of hydrogenated cottonseed oil. Such a fat, it is asserted, will not become rancid and does not, as an animal fat or lard appears to do, more readily acquire rancidity when admixed with leavening ingredients. The fat should be quite free from water, and baking powder or leavening materials, are intimately mixed therewith, either by stirring the leavening ingredients into the melted fat or mixing with the cold solid fat in a mixing machine. The fat and leavening materials are employed in such proportions that when the preparation is mixed with about 8 parts by weight of flour and with sufficient water or milk to form dough and the mass baked, the product is properly shortened and leavened. Common salt for seasoning may be mixed into the preparation so that the baker need only add the composition to flour and water or milk to form the dough. Since the baking powder is embedded in the body of lard-like fat it does not easily absorb moisture from the air and hence retains its gas-producing capacity indefinitely. The baking results attained are said to be superior to those effected by separately mixing the shortening and baking powder in the dough in the ordinary manner. The explanation offered is that the baking powder ingredients are embedded in the shortening fat and the development of the leavening gas is, for that reason, diminished or retarded in the cold dough, and hence more of the leavening action occurs when the dough is exposed to the heat of the baking oven. For this reason also, the preparation is considered to be more economical since by its use a smaller amount of the leavening agent is required. Thus, if baking soda is used in the preparation as the source of the leavening gas, the amount needed to properly leaven a given quantity of flour is stated to be about 25 per cent less than is ordinarily required, and the amount of baking acid required to react with the soda is likewise reduced.

3956. The leavening ingredients recommended are sodium bicarbonate and finely pulverized acid phosphate such as mono-calcium or mono-sodium phosphate. Acid-phosphate, particularly mono-calcium and mono-sodium phosphate, are inexpensive and efficient baking acids, but they absorb atmospheric moisture and must, therefore, be especially prepared for use in ordinary baking powder. Thus, in a stable baking powder, mono-calcium phosphate

²⁷ U. S. Pat. 1,231,114, June 26, 1917.

²⁸ U. S. Pats. 1,276,507, 1,276,508 and 1,276,509, Aug. 20, 1918.

²⁹ U. S. Pat. 1,210,940, Jan. 2, 1917.

should be used in granular form (i.e., such that it will not pass through a 156-mesh sieve), rather than in pulverulent form (i.e., such as would pass through a 200-mesh sieve). But, since the leavening ingredients are embedded in a body of shortening fat, finely pulverulent acid phosphates can be employed in Holbrook's preparation without detriment to its keeping qualities and with advantage in the baking results attained. Like the acid phosphate, the sodium bicarbonate and salt employed may be finely pulverized and dried.

In preparing the composition, the materials and proportions by weight are, for example, as follows:

	Parts		Parts
Thickened cottonseed oil.....	7	Mono-calcium phosphate.....	1.25
Sodium bicarbonate.....	1	Salt.....	1.0

3957. The leavening and seasoning ingredients are dried, finely pulverized and intimately mixed with the thickened cottonseed oil either in the hot or cold state. The proportions given are such that 1 part by weight of the improved preparation will be sufficient to properly shorten and leaven dough containing 8 parts by weight of flour, which is stated to be the proportion in which common animal shortening fat or lard is generally used.

3958. Shortening Emulsion for Food Products.³⁰ A fluid shortening mixture comprises 45-60 per cent of lard, hydrogenated cottonseed oil or other suitable edible fat emulsified in water with sodium stearate and stearic acid in proportions which render the emulsion permanent.

3959. According to Bernegau,³¹ fresh white of egg is treated at about 40° C. with freshly expressed pineapple juice (containing yeast cells), and the resulting liquid mixed with sugar, emulsified with fresh egg yolk, and sterilized by heating, yielding an emulsion suitable for blending with hydrogenated oils to produce an edible fat.

3960. Poulenc Frères³² claim that the hydrogenation of lecithin may be accomplished by the aid of common metals and their oxides, and at a temperature below that at which lecithin and hydrolecithin are decomposed, by having the catalyst in its most active condition, obtained by slow reduction in the case of the metals and by dehydration of the hydroxides at a low temperature in the case of the oxides; by vigorous stirring of the lecithin so as to expose continually fresh surface to the action of the hydrogen, and by working under increased pressure.

OTHER EDIBLE PRODUCTS

3961. Edible oil preparation in "dry emulsion" form. U. S. Pat. 1,302,486, April 29, 1919, to Dunham. Hydrogenated oils are mentioned as possible constituents. A chewing gum base is made by Dunham from rubber (with or without additions of chicle) and a hydrogenated oil such as hydrogenated peanut oil melting point 62° C. (U. S. Pats. 1,534,929 and 1,534,831, Apr. 21, 1925.)

3962. Grun. U. S. Pat. 1,505,560, Aug. 19, 1924. A method of treating fats by converting them into mixed triglycerides, such as oleo-palmito-stearin. Among the fats so treated are hardened oils.

3963. Epstein (U. S. Pat. 1,676,138, July 3, 1928) makes a food mixture suitable for preservation by homogenizing wet pressed casein 80, cocoanut oil 18.7, hydrogenated cottonseed oil 1.3.

3964. Chilling and whitening lard compounds (with illustration), U. S. Pat. 1,036,628, Aug. 27, 1912, to Humphreys, assignor to Allbright-Nell Co.

3965. Production of stable cod-liver oil emulsions which deposit no sediment on keeping. (Schwarzkopf, Ger. Pat. 419,731, Mar. 1, 1924.) Sedimentation of cod-liver oil emulsions is prevented by the addition of hydrogenated fat, e.g., 1-2 per cent of hydrogenated marine animal oil is added to an emulsion containing 40 parts of cod-liver oil, 0.5 part of gum tragacanth, 0.5 part of gum arabic, and 59 parts of water.³³

³⁰ Baker, U. S. Pat. 1,553,294, Sept. 8, 1925.

³¹ Ger. Pat. 295,351, Mar. 24, 1914.

³² French Pat. 478,193, July 22, 1914; *J.S.C.I.*, 1916, 1131.

³³ *J.S.C.I.*, Suppl., 1926, 218B.

In England one large concern is offering several grades of hardened fat ranging as follows:

	Iodine Number	Melting-point ° C.	Titer
A1.....	50	40-42	36
A2.....	85	28-30	32
C1.....	60	44-46	45
C2.....	75	35-37	36

A German firm has marketed hydrogenated marine oils with these characteristics: ¹

	Acid Number	Saponi- fication Number	Unsaponi- fiable	Iodine Number
T.....	3.5	190.7	0.33	63.9
T extra.....	3.8	190.5	0.31	36.1
C.....	3.8	190.4	0.41	18.4
C extra.....	4.4	188.4	0.52	10.4

FATTY ACIDS

	Melting-point, ° C.	Titer	Acid Number
T.....	38.5	34.6	199.7
T extra.....	45.5	43.5	199.9
C.....	48.5	47.4	198.9
C extra.....	51.8	50.5	199.9

The next table gives more details concerning these fatty acids and those of two other similar products.

PROPERTIES OF THE FATTY ACIDS OF HARDENED FISH AND WHALE OIL ² (KNORRE)

Trade Name	Appearance	Loss on Drying	Ash	Unsaponifiable	Non-fatty Material	Saponifiability	Acid Number	Saponification Number	Ester Number	Neutral Fat, Per cent	Iodine Number	Titer Test, ° C.
T fatty acids.....	Tallowy hard mass. Snow white.	0.21	0.01	0.12	0.34	99.66	187.6	203.0	15.4	7.8	69.0	42.0
O fatty acids.....	Odor, sweet. Hard.	0.15	0.31	0.46	99.54	186.1	208.8	22.7	9.1	61.1	43.0
T fatty acids.....	Crystalline. Snow white.	0.21	0.01	0.49	0.71	99.29	187.1	206.1	19.0	9.0	40.2	41.2
T extra fatty acids.	Very hard. Tallowy.	0.31	0.05	0.51	0.87	99.13	189.3	208.9	19.6	9.9	54.3	49.0
C fatty acids.....	Tallowy.	0.35	0.08	0.26	0.69	99.31	191.0	204.1	13.1	6.8	20.3	49.6
C extra fatty acids.	Hard crystalline mass.	0.15	0.10	0.31	0.56	99.44	193.0	209.1	16.1	8.4	8.9	56.1

¹ *Seifenfabrikant*, 1912, No. 31.

² *Seifen. Zig.*, 1914, 971.

CHAPTER XL

USES OF HYDROGENATED OILS IN NON-EDIBLE PRODUCTS

4000. By far the greatest consumption of non-edible hardened oils is in the manufacture of soap. Other, minor, outlets in non-edible products are in the leather industry for dressing leather, etc., in electrical work, for insulators, in the making of candles (fatty acids only), in paints to produce a flat finish, in pharmacy for ointments, and in miscellaneous uses such as the preparation of polishing and buffing materials.

HYDROGENATED OILS IN THE SOAP INDUSTRY

4001. The developments in oil hydrogenation have brought to the soap industry an innovation of fundamental importance in the domain of raw materials. The soap manufacturer, no longer well able to purchase the best grade of fats in face of the high prices paid by the margarine and other edible fat industries, has now at his disposal the means for utilizing lower grade materials in substitution for more costly stock.

4002. By hydrogenation, oils which formerly made soaps only of soft consistency, now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap-making fats. In particular, fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

4003. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. For soap making this product is satisfactory as it complies with the test for a deodorized fish oil suitable for soap making in that the odor of the original oil is not apparent when ironing laundered goods on which such soaps are used. If, however, at least with the poorer grades of oil, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation. It appears not improbable that unstable odor-forming nitrogenous impurities in fish oil add hydrogen during the hardening process and are transformed into bodies of a stable character. Moreover the current of hydrogen carries away other substances which contribute to the unpleasant smell of marine oils.

4004. As exemplifying the character of fats offered by hydrogenators to the soap manufacturer as tallow substitutes we quote the analytical results shown in the following tables:

4005. Hydrogenated fats had to fight their way into the soap-making field against much opposition, though the resistance was not as strong or as bitter as that which sought to prevent their use in food products.

4006. The opposition, though doubtless in part due to prejudice and conservatism, was chiefly based on genuine though temporary drawbacks. The degree of hydrogenation necessary to prevent the development of a fishy smell in goods laundered with hardened marine oil soap had to be ascertained. Hardened oil could not directly be substituted unit for unit for tallow. Soaps made from highly hydrogenated oils were deficient in lathering property.

4007. All these drawbacks have now been overcome and immense quantities of hardened oils, including hardened whale oil,³ are now used in soap manufacture.

4008. In the second edition of this work much space was given to the discussion of the utilization of hardened oils in the soap industry. Many formulas were offered for the preparation of different kinds of soap with various commercial types of hardened oils. This discussion is now unnecessary and much of it obsolete. Those who desire information of this kind are referred to the second edition and to the original articles cited in the footnote.⁴

4009. Jamieson⁵ states that hydrogenated oils are particularly suitable for making soaps to be used for finishing textiles.

4010. Darkening of Soap Made from Hardened Oil. Smith and Wood⁶ report that, in soaps made from hydrogenated oils, the darkening on keeping decreased with increase in the degree of hydrogenation of the raw material.

4011. Hirose⁷ also writes of the relation between the properties of the soap and the degree of hydrogenation of the oil. The surface tension and lathering power of various soaps prepared from hydrogenated soya-bean oils were studied for the purpose of comparing the oils with beef tallow. Hydrogenated soya-bean oil having an iodine value of 60-69 is the best substitute for beef tallow for the manufacture of soap, although it differs somewhat in composition. The drop

³ In April, 1929, a whale oil cargo arrived in New York valued, according to the newspapers, at \$2,000,000 and consigned wholly to one firm of soap manufacturers.

⁴ Garth, *Seifen. Ztg.*, **1912**, 1278, 1309. Heller, *Seifenfabrikant*, **1912**, No. 31. Schaal, *Seifen. Ztg.*, **1912**, 821, 846, 954, 979; *ibid.*, **1913**, 173, and in his book, "*Die moderne Toilette-seifen-Fabrikation*" (Augsburg), 1913. Full discussion and many formulas. Weber, *Seifen. Ztg.*, **1913**, 421. Cold process soap: return of fishy odor. Leimdorfer, *Seifen. Ztg.*, **1913**, 284, 310; *idem*, *J.S.C.I.*, **1914**, 206. Bergo, *Seifen. Ztg.*, **1912**, 1333; *ibid.*, **1913**, 1220. Haleco, *Seifen. Ztg.*, **1913**, 16. Hauser, *Seifen. Ztg.*, **1913**, 141. Schuck, *Soap Gaz. and Perfumer*, **1914**, 55, 419. Heller, *Soap Gaz. and Perfumer*, **1913**, 263. Ribot, *Seifen. Ztg.*, **1913**, 142. Knorre, *Seifen. Ztg.*, **1914**, 806. Müller, *Seifen. Ztg.*, **1913**, 1376; *ibid.*, **1914**, 8. Lach, *Seifen. Ztg.*, **1912**, 1245: Use of hardened Marine oils at the Fels-Naphtha works. Wilhelmus, *Seifen. Ztg.*, **1914**, 257. Use of hardened linseed oil: on this subject consult also: *Seifen. Ztg.*, **1913**, 1386, 1299; *ibid.*, **1914**, 140, 167, 231. For the use of hardened castor oil see: Garth, *Seifen. Ztg.*, **1912**, 1309, and Wilhelmus, *loc. cit.* Other articles on the general question are found in *Seifen. Ztg. passim* and particularly: **1912**, 517, 660, 720, 1003, 1230; **1913**, 312, 334, 368, 1277, 1299, 1386; **1914**, 8, 391. Kazarnovskii and Sizonenko, *Maslo-boino-Zhir. Delo*, **1923**, No. 5, 7; *C. A.*, 1929, **23**, 3590.

⁵ *Textile Colorist*, 1928, **50**, 19; *Chem. Abst.*, 1928, **22**, 1690.

⁶ *Ind. and Eng. Chem.*, 1926, **18**, 7, 692.

⁷ *J. Soc. Chem. Ind.*, Japan, 1926, **29**, 203.

number and lathering power of the soap solutions vary with the progress of hydrogenation of the fatty oils used. Drop number and specific volume of lather diminish during the first stage of hydrogenation, then rise gradually to a maximum when the oil has iodine value 60–69, beyond which they again gradually fall until the iodine value of the oil becomes zero. Iso-oleic acid formed during the hydrogenation has no injurious effect on the properties of the soap. Soaps made from unsaturated fatty acids show a fall of drop number with rise of temperature, whereas those made from saturated acids of high melting-point show the reverse effect, the maximum being generally at the temperature at which the solution becomes quite transparent.⁸

4012. The effect of adding castor-oil soap to soap made with hydrogenated herring oil was studied by Hirose. The drop number was slightly lowered. The lathering power was notably increased, the maximum being attained with 20 per cent castor-oil soap. However when more than 15 per cent of castor-oil soap is present the washing power is diminished. A formula recommended is: castor-oil fatty acid 2–3 parts, soap of hydrogenated herring oil 90 parts, castor-oil soap 10 parts.⁹

4013. Soap Making by Simultaneous Hydrogenation and Saponification.¹⁰ Soaps are made by saponifying soap-yielding materials, in presence of a hydrogenating agent, e.g., an alkali amalgam, or metallic hydrides or alloys—with or without a catalyst, e.g., reduced metals—or metal oxides, salts, or compounds. For example, a mixture of menhaden oil (566 parts) and whale oil (565 parts) is heated to 60° and emulsified with water at this temperature, and sodium amalgam in lumps (1348 parts) is added gradually to the mixture. A vigorous reaction occurs, and after addition of all the amalgam the temperature is raised to 145°–160° for a time. When saponification is complete the soap is remelted with addition of water, and salted out as usual; mercury from the amalgam settles out at the bottom of the vessel and is drawn off separately from the saline water and glycerol.

MISCELLANEOUS USES OF HYDROGENATED OILS IN NON-EDIBLE PRODUCTS

4014. Brauer. Water-binding capacity of hardened fats. *Seifen. Ztg.*, 1926, **53**, 830; *Chem. Abst.*, 1927, **21**, 663.

4015. Hydrogenated oils are used by tanners for stuffing leather and other purposes. Fish and whale oil are especially suited for this purpose. A product low in fatty acids is desired, as any large amount of free fatty acid is regarded by the tanner as likely to cause the leather to spue. Lumbard¹¹ has called attention to the use of hardened linseed and cottonseed oils, in the German leather industry. Fat-liquor of satisfactory quality can be made from a mixture of hardened oil and a sulphonated oil. Sometimes tallow is added. Leather which has been fat-liquored with such compositions can be readily japanned (for patent leather) and the japan coating is sufficiently adherent. Hydrogenated whale oil is used as a substitute for moellon. It can be employed to best advantage in the harder types of leather.

⁸ *Brit. Chem. Abst.*, 1926, 887B.

⁹ *J. Soc. Chem. Ind.*, Japan, 1927, **30**, 122; *Chem. Abst.*, 1927, **21**, 1367.

¹⁰ *Brit. Pat.* 255,508, Mar. 17, 1925, to Aische; *Suppl. J.S.C.I.*, Oct. 1, 1926, 795.

¹¹ *J. Am. Leather Chemists*, 1915, 80.

4016. A procedure given by Levinstein¹² relates to the production of compounds from hydrogenated saponifiable fats or oils and to the production therewith of compositions from waxes, fats, oils, or the like, which are soluble, miscible or emulsifiable in water without the addition of alkali. The compositions obtained are stated to be valuable in the preparation and treatment of leather, and in the textile industries, as special finishes.

4017. In carrying this method into effect, hardened oils obtained by the hydrogenation of saponifiable fats or oils, such, for example, as hardened fish oil or hardened linseed oil, are treated under certain conditions with sulphuric acid. The sulpho compounds so obtained have the property of making mineral and other waxes, oils, fats, or the like soluble, miscible or emulsifiable in water.

4018. In order to obtain these sulpho compounds, hardened linseed oil, for example, is selected, and after melting is treated with sulphuric acid until a sample from the mass gives an emulsion with water, or until a washed sample practically dissolves in ammoniacal water. The mass is then poured into water previously heated to 30° C., when the sulpho compound will separate in the form of a white pulpy mass.

4019. The following is an example of how a sulpho compound may be obtained and how such compound may be used to produce a soluble composition with mineral wax:

4020. One hundred parts of hardened linseed oil are melted and then cooled to about 35° C. under agitation. Twenty-five parts sulphuric acid (100 per cent H₂SO₄ monohydrate) are then added gradually and the temperature is kept between 40° to 45° C. until a washed sample is practically soluble in hot water. The whole is then run into a salt solution (10° Tw.) which has been heated to a temperature of 30° C., is well stirred, and then allowed to settle, after which the salt water is drawn off. The washing with salt water is again repeated until the mineral acid has been removed, or the mineral acid may be neutralized with alkali. The sulpho acid of hardened linseed oil, thus obtained, when melted and mixed with equal parts of paraffin wax gives a composition which is practically soluble in hot water without the addition of alkali.

The hardened oils can be sulphonated when mixed with oils or greases, but the property possessed by the product of making waxes miscible or soluble or emulsifiable in water without neutralizing the sulpho acid or without any addition of alkali, appears to be to some extent diminished.¹³

4021. Hydrogenated oils and their soaps (metal salts) have found some application in the manufacture of lubricants. Their use is, chiefly, to confer body on a thin mineral lubricant.

4022. Lubricants produced from fatty (and mineral) oils by hydrogenation and polymerization in an electric field are described in Chapter LI of this volume. Ellis¹⁴ produced a polymerized and hydrogenated oil by a different method, the chief object of which, however, was to produce a soap with free lathering properties. The process is applicable to the manufacture of lubricants.

4023. The polymerization is carried out by protracted heating preferably in the absence of air until the iodine number has been reduced to as low a degree as is feasible. This reduction depends upon the oil which is being treated. Fish or whale oil may have the iodine number readily reduced by polymerization to about 80 or 90. Such products usually still possess a fishy odor and by hydrogenating to an iodine number of 40 or 50 the odor is eliminated and, in some cases, the taste becomes fairly bland. Ellis has prepared soaps from such products and finds them to possess relatively good lathering properties and to yield soaps in other respects of quite satisfactory quality.

4024. Further details of the joint result of polymerizing and hydrogenating a fatty oil are described in a later patent.¹⁵ Fatty acids and unsaturated oils such as the glycerides containing more especially two or more double bondings or olefine groupings are capable of polymerization at elevated temperatures resulting in a thickening of the oil due not so much to the formation of stearin as to the formation of oil complexes by the union of oil molecules

¹² U. S. Pat. 1,185,414, May 30, 1916.

¹³ Brit. Pat. 16,890, July 16, 1914; *J.S.C.I.*, 1915, 913; *Chem. Abst.*, 1916, 10, 288.

¹⁴ U. S. Pat. 1,151,002, Aug. 24, 1915.

¹⁵ U. S. Pat. 1,178,142, Apr. 4, 1916.

one with another, usually denoted by a profound reduction of the iodine number and other changes. In this manner castor, fish, whale, cotton, corn, linseed, rape and tung oil and the like may be polymerized to differing degrees and by such polymerization a thickening of the oil usually occurs which produces a body of viscosity that enables one to obtain by hydrogenation, a product containing a fatty derivative of good texture or consistency. The product may be used in making lubricants, or may be sulphonated by treatment with sulphuric acid or soaps may be prepared by saponification with alkalies.

4025. When catalyzers such as nickel are employed, it is preferred first to polymerize the oil at about 250° C. and then to reduce the temperature and harden by means of hydrogen at a temperature around 200° C.

4026. Hardened or hydrogenated oil produced by simple hydrogenation is not capable of yielding soaps having as free lathering qualities as often as desired, while some grades of the polymerized and hardened hydrogenated oil show superior lathering qualities when converted into soap.

4027. To remove the odor from fish and whale oil by hydrogenation requires a considerable conversion to stearin. Usually it is necessary to reduce the iodine number of fish oil to 40 or 50 in order to convert the unsaturated bodies such as clupanodonin which are supposed to be more or less odor-producing into more saturated or entirely saturated bodies rendering the oil free from disagreeably fishy odor. But hydrogenation to this point produces so large a proportion of stearin which lathers freely as a soap only in very hot or boiling water that the product when used with cold or slightly warm water is deficient in lathering and consequent detergent properties. By polymerization the property of cold lathering existent in the soaps produced from normal fish oil is to a considerable degree present in the polymerized oils and any further hardening which may be desired and which is secured by hydrogenation does not impair these lathering qualities to any material degree in connection with the production of fats for making hard soaps. Hence, polymerization enables the production from oils and fats of a thickened or hardened product without the necessity of carrying hydrogenation forward to such a degree that the lathering properties of the soap are seriously impaired.

4028. The following procedure will serve to illustrate the foregoing: Whale oil was heated in an atmosphere of carbon dioxide for sixteen hours at a temperature between 250° and 270° C. The final product was viscous and the fishy odor was largely eliminated. The iodine number of the oil before heating was 135.5 and that obtained after heating had an iodine number of 89.7. The polymerized oil was treated with hydrogen in the presence of nickel material as a catalyzer and a product was obtained which did not appear to have any very definite melting-point. Changes in temperature between quite wide ranges did not appear to affect the consistency very materially. It melted completely at about 37° C. and the iodine number was found to be 65.9. A quantity of the whale oil which had not been polymerized was hydrogenated under the same conditions and soaps prepared from both the products by saponification with alkali under like conditions. The soap obtained from the hydrogenated whale oil had almost no lather in cold water, while the polymerized and hydrogenated product gave a copious lather in water of the same temperature. The fats as well as the corresponding soaps were free from any fishy odor. It appears to be an approximately correct statement that the lathering qualities of a soap depend on the melting-point of the fats from which it is made. A soap made from oleic acid lathers rather easily in cold or slightly warm water, while that made from stearic acid requires a temperature of nearly 80° C. to develop a satisfactory lather.

4029. Hydrogenated Marine Oil in Lubricant. Rolfsen¹⁶ adds 0.5–10 per cent of hydrogenated marine (e.g., whale) oil to mineral oil to form a lubricant for internal combustion engines.

4030. Fox¹⁷ notes that practically all the semi-drying oils are capable of use for lubricants, as they can be hydrogenized and converted into non-drying oils. He prepared a lubricating oil from hydrogenized soya-bean oil mixed with 14 per cent of mineral oil. A lubricating grease, similarly made, was used in the gearbox of a motor car for nearly a year.

¹⁶ Brit. Pat. 258,606, Nov. 17, 1926 (Norwegian date, Nov. 18, 1925); U. S. Pat. 1,717,939, June 18, 1929.

¹⁷ J.S.C.I., 1918, 304R.

4031. Ellis¹⁸ incorporates hydrogenated oil and pulverulent material. The product may take either of two forms: (1) a solid cake or semisolid coherent mass and (2) a comminuted or pulverulent product. The solid cake may be used for a variety of purposes such as buffing and grinding, lubricating, polishing and the like. A lubricating powder may be made, for example, from equal weights of hydrogenated oil and graphite. A buffing or grinding composition may be produced from hydrogenated oil and an abrasive powder such as crocus or carborundum and emery. A tailor's chalk may be made by melting hydrogenated cottonseed oil of m.p. 60° C. with a quantity of talc.

4032. The hydrogenation process enables olein (oleic acid) to be prepared in two ways according to Dubovits¹⁹ either by treating hydrogenated fatty acids of a titer of 40 to 46 in the usual way to separate stearin and olein or to hydrogenate cheap oil of high iodine number to bring the iodine number to about 80 or 90 or approximately that of olein, and saponify this product. The resulting olein contains only a few tenths of a per cent of unsaponifiable matter and a few per cent of neutral fat. The liquid fatty acid contains highly unsaturated components in spite of the iodine number of 80 to 90.

4033. The application of hardened oils in the candle industry is noted by Bontoux²⁰ who states that the operations of pressing or distillation, impose a limit on the degree of hardening practicable.

4034. In splitting fats with aromatic sulpho-fatty acids, the color of the resulting product is improved by using partially hydrogenated castor oil, containing hydroxyl, for preparing the dissociating agent. One part each of hardened castor oil and naphthalene are ground to a powder and treated with 4 parts of commercial sulphuric acid at a temperature below 20° C. The resulting product is poured into 8 parts of water and the upper layer which forms is collected and used as a fat-splitting agent.²¹

4035. Starrels²² prepares fatty acids by hardening a fatty oil to a high melting-point, as, for example, to about 60° or 62° C., and an iodine number of from zero to 2 and thereby substantially completely converting the olein into stearin, also forming various isomers of high melting-point.

4036. The material is saponified by the Twitchell process or any of the other fat-splitting processes yielding glycerine and high melting-point fatty acids. The latter mixture is then dissolved in a solvent medium, as, for example, alcohol or gasoline, and, on cooling, the free fatty acids are separated in a state of purity, leaving in solution the greater part of the coloring agents. An example is the following: Corn oil was hydrogenated, using nickel catalyzer, until the melting-point was about 62° C. It was then subjected to the Twitchell process and the fatty acids obtained. These were brown in color. Approximately equal parts of denatured alcohol and the fatty acid were incorporated and heated to form a homogeneous solution which takes place rather readily at temperatures approaching the boiling-point of alcohol as the fatty acid is relatively soluble in alcohol. The solution was cooled until practically all of the fatty acid had separated, when the material was pressed and a brown extract containing the hydrocarbons and coloring matters was removed leaving a white fatty acid of very high saponification value and acid number showing that the unsaponifiable material formed by hydrogenation had been eliminated.

4037. According to a method of the Reuter Process Co.,²³ in the production of fatty acids by boiling glycerides with organic catalytic hydrolyzers, the hydrolysis is effected in a number of stages, in each of which stages a fraction of the total amount of hydrolyzer is added, the mixture being allowed to settle after each boil and a dark-colored intermediate layer of impurities is removed, after which more hydrolyzer is added and boiling resumed. Air is excluded from the saponification tank. The fatty acids thus produced, and soap and candles made therefrom, after aging for ten days after making, do not darken substantially in color on exposure to air and light. Glycerides used in this process may be the following, separately or collectively: Beef and mutton tallow; horse, hog, and butter fats and their greases;

¹⁸ U. S. Pats. 1,276,507, 1,276,508 and 1,276,509, Aug. 20, 1918.

¹⁹ *Seifen Fabrikant*, 1915, 137 and 157, *Seifen. Ztg.*, 1915, 459.

²⁰ *Matières Grasses*, 1914, 4194; *Seifen. Ztg.*, 1914, 987.

²¹ Ger. Pat. 298,773, Vereinigte Chem. Werke, A.-G.; *American Perfumer*, 1918, 382.

²² U. S. Pat. 1,209,512, Dec. 19, 1916; *cf.*, Brit. Pat. 155,782, Dec. 23, 1920, to same patentee; C. A., 1921, 1826. A further development is covered by Starrels' U. S. Pat. 1,701,703 according to which the fatty acids are esterified with alcohol and the esters distilled. Thus high-grade soaps may be prepared from low-grade oils.

²³ Brit. Pat. 9,394, June 26, 1915.

whale, menhaden, fish, coconut, peanut, linseed, cottonseed, palm, palm-kernel, and soybean oils; and the hydrogenation products of corn oil, linseed and cottonseed oils, fish oil, etc.

4038. Highly hardened oil such as a thoroughly hardened cottonseed oil is used by Ellis ²⁴ to produce a flattening effect in paint compositions so that the surface will dry to a matt finish.

4039. Hydrogenated castor oil is used by Cordes ²⁵ as an insulating or impregnating material for telephone condensers. In manufacturing these condensers, long strips of paper are laid on strips of tin-foil, the two strips are then rolled up, and the coils thus formed are pressed into a rectangular shape and dried either with or without the use of a vacuum. The coils of paper and tin-foil are then mounted in frames, the frames with the coils thereon are placed in a vacuum-impregnating receptacle containing the hydrogenated castor oil and the coils are heated, for which purpose the receptacle has a heating jacket which receives steam at a pressure of about 2 atmospheres. The molten fat is in this way caused to penetrate between the paper and the tin-foil and the moisture is expelled by the heat in the form of bubbles. The vessel is subsequently sealed hermetically, and the extraction of moisture continues until the last trace has been removed from the paper, this part of the process occupying from two to four hours. After the moisture has been thoroughly extracted, cold water is introduced into the jacket. Owing to the high dielectric properties of the impregnating material, it is possible to obtain the same effects with condensers, which are only half as large as those necessary with the use of paraffin.

4040. In pharmacy hydrogenated oils have been used in the preparation of liniments, ointments, cerates, plasters, suppositories and pessaries. Lackey and Sayre made an elaborate investigation of the pharmaceutical availability of hydrogenated corn oil. They note as an advantage the excellent keeping qualities of hardened oils.²⁶

4041. Hardened Oil as Vehicle in Oxidizing Oils. According to Eisenstein ²⁷ linseed or other unsaturated oils are mixed with hardened sunflower oil so as to produce a solid. This is treated with an oxidizing agent, such as manganese resinate. After the completion of the oxidation the oxidized product is separated by liquation.

4042. Ogawa and Nishiuchi. On the electrical uses of squalene hydrocarbon. *Res. Electro-tech. Lab.*, Japan, 1923, **143**. Hydrogenated squalene (from shark liver oil) is recommended as a high-grade insulating oil.

²⁴ U. S. Pat. 1,173,183, Feb. 29, 1916.

²⁵ U. S. Pat. 1,241,926, Oct. 2, 1917. See also Nos. 1,276,507, 1,276,508 and 1,276,509 issued Aug. 20, 1918, to Ellis.

²⁶ *J. Am. Pharm. Assoc.*, 1917, **6**, 349.

²⁷ U. S. Pat. 1,564,33, Dec. 8, 1925; *Chem. Abst.*, 1926, p. 515.

CHAPTER XLI

INDUSTRIAL HYDROGENATION OF NAPHTHALENE, ANTHRACENE, PHENANTHRENE AND THEIR DERIVATIVES

4100. The quantity of naphthalene obtained as a by-product has been much in excess of any demand for the hydrocarbon. The products of hydrogenation of naphthalene have, however, several outlets as solvents, as fuels and as intermediates in the dye industry. Naphthalene and its immediate derivatives hydrogenate more readily than benzene and its compounds; with the additional feature of interest that when hydrogen is added in only one nucleus of the naphthalene structure there arise bodies which have properties both of those exhibited by the aromatic and the hydro-aromatic or alicyclic nucleus. In other words the hydrogenated nucleus resembles a fatty radicle in its reactions, whereas the non-hydrogenated nucleus manifests aromatic properties.

4101. A reference to the processes given in paragraphs 2066–2071 shows that catalytic hydrogenation of naphthalene in the laboratory can be effected, without special difficulty, by most of the familiar procedures. All these methods, however, require a raw material of a high degree of purity, since the sulphur compounds present in commercial naphthalene, especially thionaphthene, poison the catalyst. The methods of purification used by the laboratory workers were not as desirable for industrial application. This was the situation when the blockade having caused in Germany a shortage of motor fuels, solvents and lubricating oils, the attention of German industrial chemists was turned to the problem of hydrogenating naphthalene on a large scale.

4102. Purification of Commercial Naphthalene. Evidently, methods of purification of the crude naphthalene needed some simplification and cheapening. Various expedients were tried and the progress towards efficacy and simplicity can be followed by studying the methods described in the following paragraphs.

4103. Purification by Fusion with Porous Material.¹ Naphthalene is hydrogenated by treating while in the fused state and at a temperature above 100° C. with hydrogen in the theoretical quantity and in the presence of a catalyst. Decahydronaphthalene or other less highly hydrogenated products are obtained, and these products are suitable as lamp, motor, and lubricating oils, etc. In an example, naphthalene is purified by *fusion with fuller's earth or other porous material* and, after separation, is mixed with a catalyst consisting of finely divided nickel precipitated on a porous material. The spongy mass so obtained is treated

¹ *Chem. Abst.*, 1920, 14, 3674; Brit. Pat. 147,474, July 8, 1920, to Schroeter.

at a temperature of 120°–150° C. with hydrogen under 3–100 atmospheres pressure.

4104. Purification by Fusion with Metal under Pressure.² Naphthalene to be hydrogenated is preliminarily purified by treatment in the fused state with *finely divided metals* such as nickel or iron, or with *readily fusible metals or metal alloy* such as sodium or potassium. The materials are stirred together in an atmosphere of hydrogen under pressure and maintained at a temperature of 100° C., and the purified naphthalene is preferably distilled off under reduced pressure.

4105. Purifying (Desulphurizing) and Hydrogenating Hydrocarbons. A process closely resembling that used for the treatment of naphthalene has been proposed for the simultaneous desulphurization and hydrogenation of such substances as heavy mineral oils, naphthalene, anthracene, coal distillates and coal slimes.³ The raw material is heated under pressure in an atmosphere of hydrogen in the presence of sodium, potassium, rubidium or caesium. Fuller's earth, diatomite, carbon, magnesia or iron powder may be used to promote the reaction. From a mixture of coal and tar oil treated under 100 atmospheres pressure at 430° C. motor spirit may be obtained. At 300° C. under 100 atmospheres pressure anthracene yields the decahydride and naphthalene the tetrahydride when treated with sodium and fuller's earth.⁴

4106. Mineral Oil Substitute for Use in Electric Switches and Transformers.⁵ A modification of this process, or rather an application of it to tar oils, is for the purpose of producing an oil suitable for use in electric switches and transformers. It is also mentioned that agitation of lignite tar fuel oil with sodium above 100° C. produces an oil suitable for use as a lubricant.

4107. Purification by Fusion with Metal Compound of Non-acid Radical.⁶ Naphthalene to be hydrogenated is subjected to preliminary purification by fusion with a *metal compound* in which the metal is loosely bound to a non-acid radical, e.g., sodamide, potassamide or carbides such as aluminum or calcium carbide. The metal compound may be mixed with finely divided or porous materials.

4108. Purification in the Vapor Phase.⁷ Naphthalene to be hydrogenated is preliminarily purified by treatment in the *vapor phase* with finely divided or readily fusible metals or metal alloys or with such metal compounds in which the metal is loosely bound to a non-acid radical; the purifying materials may be mixed with finely divided or porous materials such as fuller's earth. The naphthalene vapors may be passed through several layers of the purifying materials, or through

² *Chem. Abst.*, 1920, **14**, 3675; Brit. Pat. 147,476, July 8, 1920. Addition to 147,474, to Schroeter.

³ Brit. Pat. 213,661, Jan. 2, 1923, to Hofsass and Internationale Bergin Compagnie voor Olie en Kolen-Chemie.

⁴ *Chem. Abst.*, 1924, **18**, 2426.

⁵ Ger. Pat. 299,691, Feb. 7, 1927, to Tetralin G.m.b. H.; *J.S.C.I.*, 1920, **39**, 440A.

⁶ *Chem. Abst.*, 1920, **14**, 3675; Brit. Pat. 147,488, July 8, 1920. Addition to 147,474; U. S. Pat. 1,680,070, Aug. 7, 1928, to Schroeter.

⁷ Schroeter and Tetralin Ges., *Chem. Abst.*, 1920, **14**, 3675; Brit. Pat. 147,580, July 8, 1920; Ger. Pat. 299,012, Aug. 2, 1916; *J.S.C.I.*, 1920, 743A.

the fused material maintained if desired in a finely divided state, as for example, in a "lixiviating" column; thus the vapors may be passed through a vessel filled with melted sodium and maintained at 150° C., and afterwards condensed and treated with hydrogen at a temperature above 100° C. in the presence of a nickel catalyst; or the vapors may be passed through a tower containing finely divided nickel or iron mixed if desired with fuller's earth, or through which liquid metals or metal alloys are maintained in circulation by means of a pump. By stopping the hydrogenation at the desired point, tetrahydronaphthalene may be obtained.

4109. Purification in Solution.⁸ Commercial naphthalene is *dissolved in an organic solvent* and after preliminary purification, and with or without removal of the solvent, is treated with hydrogen in the presence of a catalyst. Suitable purifying materials are finely divided or readily fusible metals or metal alloys, or metal compounds in which the metal is loosely bound to a non-acid radical, either alone or mixed with finely divided or porous materials such as fuller's earth. In an example, commercial naphthalene is dissolved in tetrahydronaphthalene and treated with metallic sodium at a temperature of 150°–200° C.; after distillation from the residue the purified naphthalene in solution is treated with hydrogen in the presence of a catalyst.

4110. Finally, a fairly simple and inexpensive procedure was adopted. This consists in "stirring molten naphthalene at temperatures of about 150°–200° C., with a small percentage of a highly absorbent substance, such as fuller's earth, kieselguhr, absorbent charcoal, talc, etc. In addition easily fusible metals such as sodium or potassium may be employed, in which case smaller quantities of the absorbent substance are required. Reduced metals, such as nickel or iron, naturally in a very finely divided condition, or substances like sodamide, calcium carbide, etc.—a metal combined with a non-acid radical—assist the purification of naphthalene up to a standard permitting subsequent hydrogenation. After a relatively short contact with the purifier the naphthalene is filtered from, or preferably, distilled off the spent material into the hydrogenation autoclaves. The pre-treatment may have been carried out in a hydrogen atmosphere, but if distillation be subsequently practiced this is effected *in vacuo*."⁹

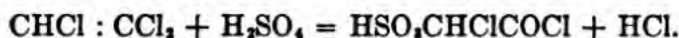
4111. Purification of Naphthalene by Another Process. Guyot¹⁰ describes a very different method for the purification of naphthalene to prepare it for hydrogenation. Naphthalene itself is unaffected by treatment at 100° C. with 7 per cent of chlorosulphoacetyl chloride ($\text{HSO}_2\text{CHClCOCl}$) but the sulphur compounds present as impurities are changed and rendered soluble in water, so that they can be removed by washing. Sodium hydroxide is added and the puri-

⁸ Schroeter, Brit. Pat. 147,747, July 8, 1920. Addition to 147,580; *Chem. Abst.*, 1920, **14**, 3675; *Chem. Abst.*, 1921, **15**, 96; Ger. Pat. 299,013, Aug. 2, 1916; *J.S.C.I.*, 1920, 743A. Crude anthracene is purified by treatment with tetralin and an agent for removal of carbazole (e.g., pyridine, potassium hydroxide or methylethyl ketone. Ger. Pat. 472,183, Feb. 6, 1922, to Deutsche Hydrierwerke A.-G.

⁹ *Chem. Age*, 1922, **30**, 4, 173. See German patents to Tetralin Ges. m. b. H. (B) 324,862, Aug. 1, 1915, and (C) 324,863, May 14, 1916. This process of purification and hydrogenation is described in Schroeter's U. S. Pat. 1,582,310, Apr. 27, 1926.

¹⁰ *Chimie et industrie*, Apr., 1928. Spec. No. 408; *Chem. Abst.*, 1928, **22**, 4522.

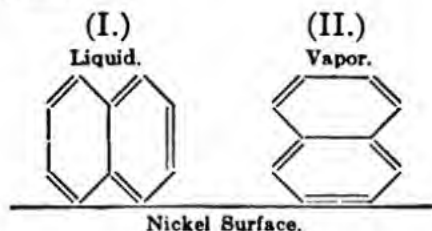
fied naphthalene is distilled.¹¹ The reagent is prepared by the action of 100 per cent sulphuric acid on trichlorethylene:



4112. Hydrogenation of Purified Naphthalene. Naphthalene treated as described in paragraph 4110 and showing no red coloration when rubbed with strong sulphuric acid is passed to the hydrogenation autoclaves. Simple distillation from the purifying vessels directly into the autoclaves has been stated to be the most suitable procedure. A proportion of a nickel catalyst, say 5 per cent, is added, and hydrogen passed under conditions of temperature and pressure of 200° C. and 15 atmospheres respectively. Hydrogenation is rapid at first, and as the reaction is exothermic, little or no heat is required to be supplied to the autoclaves, if sufficient heat insulation is provided to compensate for radiation losses from the surfaces of the autoclaves. Rapid agitation must be maintained in order to insure intimate contact between naphthalene, hydrogen and catalyst.

4112A. Many types of autoclaves are possible, and detailed description is unnecessary, but since leakage of hydrogen around glands and stuffing boxes associated with mechanical agitation fittings, is very considerable and costly to the process, some of the types in which the stirring gear, motors included, are entirely enclosed, should be very useful. This is especially the case when the operations are to be effected at pressures around 15 atmospheres, since the problem of hydrogen loss received great attention in the development of the oil-hardening process, where much lower pressures, and, presumably, much lower hydrogen losses, obtained.^{11a}

4113. Ellis¹² hydrogenates naphthalene and other aromatic compounds by circulating them in the *liquid* form, with heating, in presence of a catalyst and of hydrogen. The catalyst, which may be carried on granular charcoal, may be composed of nickel, cobalt, iron, platinum, palladium, with copper, manganese, titanium, molybdenum, vanadium, thorium, zinc or other oxides or silicides, with or without selenium or tellurium oxide. The importance of hydrogenation of naphthalene in the *liquid* state as a means of securing directly, notable yields of decalin (decahydronaphthalene) has been pointed out by Lush (see para. 4120). An explanation offered by Lush of the selective hydrogenation of naphthalene leading to the production of tetralin (tetrahydronaphthalene) exclusively in the vapor phase and decalin in the liquid phase may be found in the different manner in which naphthalene is oriented at the nickel surface in the two cases. Thus in the liquid phase naphthalene perhaps is oriented as in (I), and in the vapor phase as in (II), a difference sufficient to warrant the expectation of the formation of different compounds.^{12a}



¹¹ French Pat. 602,408; Nov. 26, 1924, to Cie. de prod. chim. et électromét. Alais, Frogeset Camargue.

^{11a} *Ibid.*, 174. See also Ger. Pat. 324,861, Feb. 25, 1915, to Tetralin G. m. b. H.

¹² U. S. Pat. 1,345,589, July 6, 1920; *Chem. Abst.*, 1920, 14, 2645.

^{12a} *J.S.C.I.*, 1927, 46, 454T. Cf. para 413.

4114. Catalysts. In general, catalysts suitable for hydrogenation of oils may be used. The life of the catalyst depends on the degree of purification of the naphthalene.

4115. The Tetralin G. m. b. H. favors nickel on a carrier of fuller's earth but has also patented a "nickel oxide" catalyst from basic nickel carbonate which is said to have greatly enhanced activity.

4116. The hydrogenation proceeds smoothly and quickly for the formation of tetralin, but the further hydrogenation to decalin requires higher temperatures and pressures and therefore more costly apparatus.

4117. Oxide Catalysts in Hydrogenation of Naphthalene. The method for hydrogenating naphthalene in the presence of finely divided nickel is modified by replacing the nickel by more efficient catalysts consisting of mixtures of the oxides, hydroxides, or salts of metals, such as nickel, cobalt, iron, manganese, or copper, with or without suitable carriers. Tetrahydronaphthalene is rapidly produced in the presence of nickel carbonate, formate, or borate.¹³

4118. Wimmer¹⁴ makes a catalyst by heating an organic salt, such as nickel formate, in a saturated glyceride with hydrogen. The product permits the reduction of naphthalene at 180° C., by hydrogen under a pressure of 15 atmospheres, to decahydronaphthalene.

4119. Preparation of Tetrahydronaphthalene—Hydrogenation in the Vapor Phase.¹⁵ A mixture of naphthalene vapor and hydrogen is passed over a mixture of nickel and copper oxides without employment of increased pressure; a smooth formation of tetrahydronaphthalene is observed at 140°–150° C. A modified process involves the use of mixtures of the oxides of manganese, nickel, and copper, including such as are mainly composed of the first-named. In a third process, catalysts are employed in which the oxides of nickel, copper, or manganese are completely or partly replaced by an oxide of the rare earth metals, particularly thorium or cerium oxide.

4120. Lush¹⁶ describes the hydrogenation of naphthalene to tetrahydronaphthalene by means of a nickel catalyst at a temperature sufficiently high to avoid condensation of the naphthalene on the catalyst. It has been found that if condensation occurs some decahydronaphthalene and by-products are also formed.¹⁷ Lush conducted numerous experiments on the hydrogenation of naphthalene in the vapor phase at temperatures ranging from 100°–200° C. and found that tetralin was produced exclusively. Figure 94 shows the effect of temperature on the hydrogenation of mixtures of naphthalene and tetralin from which it will be noted that the percentage of decalin increases up to 200° C. At 230° dehydrogenation takes place. Figure 95 shows the effect of variation in hydrogen pressure, indicating an increased production of decalin with increase in pressure.

¹³ Brit. Pat. 172,688, Aug. 11, 1920 (addition to 147,474), to Schroeter and Tetralin Ges. m. b. H.; *J.S.C.I.*, 1923, **42**, 8A.

¹⁴ Wimmer, *J.S.C.I.*, 1920, 743A; Ger. Pat. 300,052, Mar. 14, 1915.

¹⁵ Aktien Gesellschaft für Anilinfabrikation. Ger. Pats. 298,541, 298,553, 301,275; from *Chem. Zentr.*, 1921, ii, 559; *J. Chem. Soc.*, 1921, **119** and **120**, i, 333.

¹⁶ Brit. Pat. 304,403, Nov. 4, 1927, to Tech. Research Works, Ltd., and Lush.

¹⁷ *Chem. Age* (London), 1929, **20**, 188. See also paras. 2066–2069, this book.

A mixture of naphthalene and tetralin, allowed to flow over a nickel catalyst at 160° C. and at various pressures, yields decalin in notable proportion, ranging from 9.2 per cent at atmospheric pressure to yields above 40 per cent at a pressure of 300 lbs. See Figure 96. From the foregoing Lush has drawn the following conclusions: (a) When naphthalene is catalytically hydrogenated in the vapor phase tetralin is formed exclusively. (b) When either liquid naphthalene or tetralin is hydrogenated at the same temperature and pressure decalin is

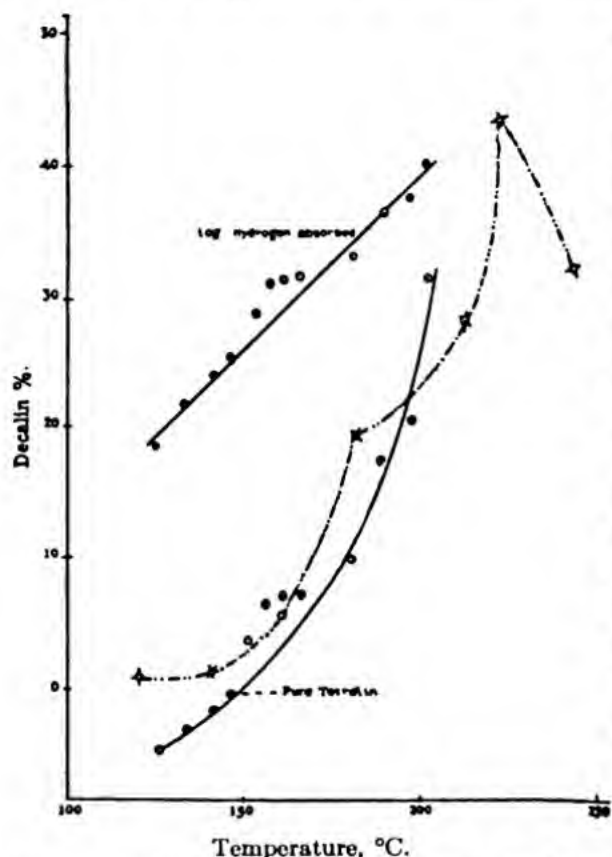


FIG. 94.—HYDROGENATION OF MIXTURES OF NAPHTHALENE AND TETRALIN.

Effect of temperature (Lush, J.S.C.I., 1927, 46, 454T.)

a poor catalyst, but the potassium sodium alloys are exceptionally active. The alloys can be prepared by fusing sodium at 250°–360° C. with the equivalent of potassium hydroxide.

4122. Iodine as Catalyst.¹⁹ Naphthalene when heated for one hour with 1 per cent of iodine at 550° C. in presence of hydrogen at about 170 atmospheres pres-

formed. (c) The effect of hydrogen pressure on the decalin thus obtained is such as leads Lush to the conclusion that decalin would not be formed in the vapor phase.^{17a}

4121. Hydrogenation of Crude Naphthalene, Sodium Catalyst. A process of some promise is disclosed in French Pat. 559,787 and described by Guyot.¹⁸ Crude naphthalene can be hydrogenated to tetrahydronaphthalene at 300° C. under a pressure of 100 atmospheres of *unpurified* hydrogen, in presence of metallic sodium as a catalyst. It is, however, essential that the reactants be dry. Sodium is unaffected by the usual catalyst poisons, which should be true, also, of all catalysts which are liquid at the operation temperature, provided there is brisk agitation and also that an inert material is present to give large contact area, e.g., magnesia or kieselguhr. Potassium alone is

^{17a} J.S.C.I., 1927, 46, 454T. Cf. para. 4113, also para. 413.

¹⁸ *Chimie et industrie*, 1928, Apr. Spec. No. 410; *Chem. Abst.*, 1928, 22, 4522. Contrast para. 4127. Ger. Pat. 473,457, May 7, 1925; *Chem. Abst.*, 1929, 23, 2986. See also para. 2066, this book.

¹⁹ Fischer and Niggemann, *Ges. Abhandl. zur Kenntnis der Kohle*, 1917, I, 231–236. *Chem. Zentr.*, 1919, 90, II, 585–586.

sure is completely liquefied to an oil with a bluish fluorescence with simultaneous separation of a "mirror" of carbon, the separation of carbon being favored by an excess of pressure. Under 50 atmospheres hydrogen pressure separation of carbon begins above 800° C., with 50 atmospheres at 800° C., 100 atmospheres at 550° C., and 170 atmospheres below 550° C. The hydrogenized oils so prepared solidify after standing for several days.

4123. Berginization of Naphthalene, Anthracene, etc.

According to Spilker and Zerbe²⁰ treatment of naphthalene in an autoclave with hydrogen at 100 atmospheres (initial) and 470° results in transformation of about one-third into hydronaphthalenes, mostly tetralin. At lower temperatures and pressures less is attacked; at higher temperatures, hydrobenzenes and other decomposition products are formed. Similar results are obtained in presence of aluminum chloride, the yield of higher-boiling products being somewhat greater. Hydrogenation of anthracene at 450° and initial pressure of 75–80 atmospheres yields a completely liquid product of mixed hydroanthracenes. Phenanthrene and acenaphthene under the same conditions yield 30 and 90 per cent respectively, of hydrogenated liquid mixtures. Fluorene yields 30 per cent of liquid hydrofluorenes when treated at 465°; carbazole remains unattacked under the same conditions.²¹

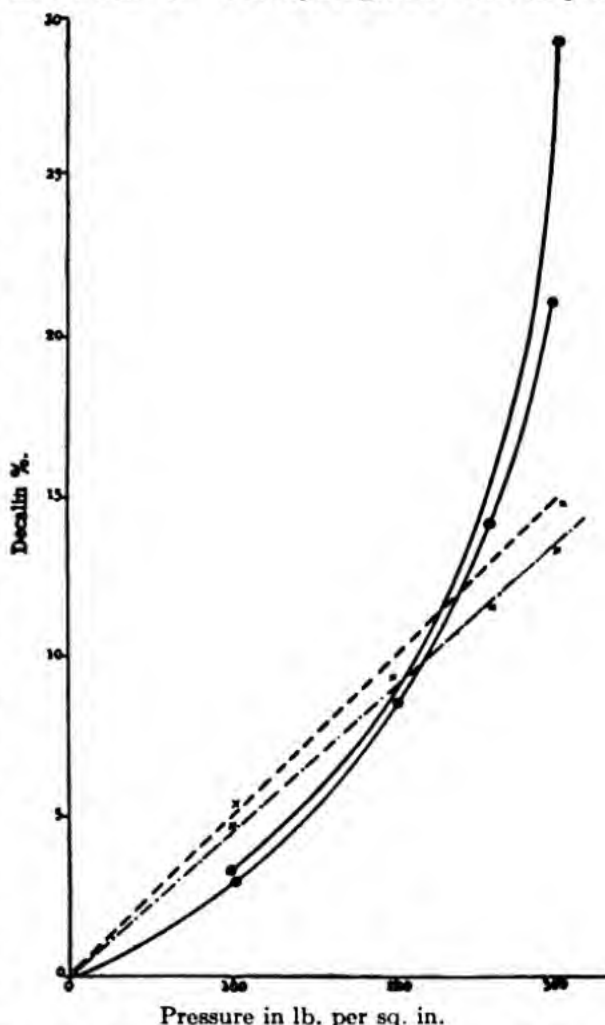


FIG. 95.—HYDROGENATION OF MIXTURES OF NAPHTHALENE AND TETRALIN.

Effect of pressure. Temperature, 200°. (Lush, J.S.C.I., 1927, 46, 454T.)

4124. Optimum Conditions for Naphthalene, etc., Hydrogenation. According to Kling and Florentin the optimum conditions for hydrogenation by berginization of naphthalene are a yield of 10 per cent per hour at 100 kilograms per

²⁰ *Z. angew. Chem.*, 1926, **39**, 1138. These studies were continued by Hofmann and Lang (*Brennstoff. Chem.*, 1929, 203) who worked on benzene, toluene, cyclohexane, cyclohexene, ethylene, and pyridine.

²¹ *Brit. Chem. Abstr.*, 1926, 939B.

cm. pressure and 485° C. For anthracene the temperature is 440° C. The reaction can be accelerated by catalysts.²²

4124A. Hugel and Friess²³ were unable to confirm Kling and Florentin's observation²⁴ that naphthalene can be hydrogenated by berginization without catalysts.

4125. Kling and Florentin described the hydrogenation of naphthalene (and anthracene) at high pressure and at high temperature in presence of non-hydrogenating catalysts. The catalysts were aluminum chloride and ferric chloride;

the threshold temperature of hydrogenation varied somewhat with the pressure.²⁵

4126. Prudhomme²⁶ passes a mixture of naphthalene vapor and hydrogen or water-gas through a tube packed with Laming's material at 190°–225° C., then over nickel-pumice. The product, which varies with the conditions, consists of hydronaphthalenes from dihydro- to decahydronaphthalene.

4127. Non-catalytic Hydrogenation of Naphthalene and Its Derivatives.²⁷ One process utilizes the hydrogen generated by action of water on sodium. Water is allowed to act slowly on a mixture of alkali metals with a solution of naphthalene or its derivatives in an indifferent solvent. For example, by slow addition of water to a mixture of naphthalene and metallic sodium in solvent naphtha at 145°, tetrahydronaphthalene is obtained.

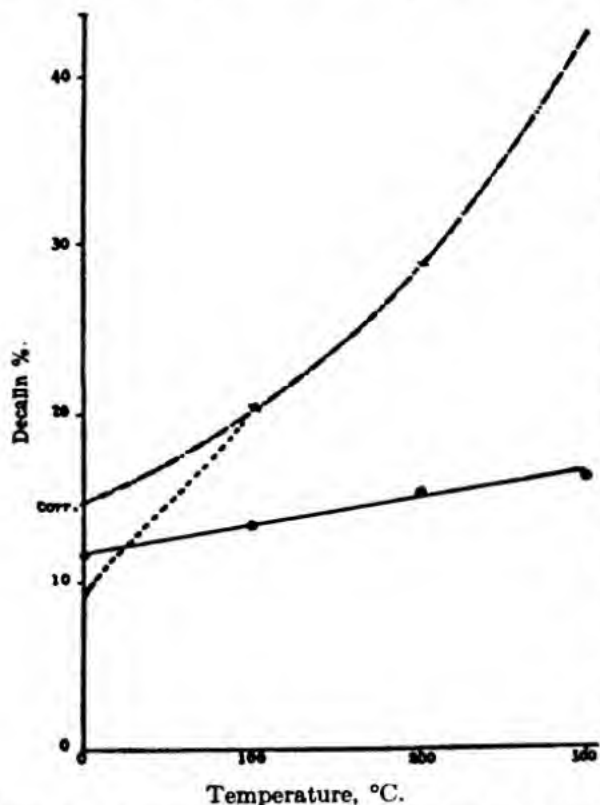


FIG. 96.—HYDROGENATION OF MIXTURES OF NAPHTHALENE AND TETRALIN.

Effect of pressure. Temperature, 160°. (Lush, J.S.C.I. 1927, 46, 454T.)

When a mixture of aliphatic hydrocarbons of boiling-point 115–120° is used in place of solvent naphtha, dihydronaphthalene is obtained. α -Naphthylamine is similarly hydrogenated to tetrahydro- α -naphthylamine, and β -naphthol ethyl ether to tetrahydro- β -naphthyl ethyl ether, an oil, boiling-point 155°/128 mm., having a pleasant odor. It is

²² Bull. Soc. Chim., June, 1927.

²³ Bull. Soc. Chim., 1927, 41, 1185; Chem. Abst., 1928, 22, 416.

²⁴ Para. 4124.

²⁵ Compt. rend., 1927, 184, 822.

²⁶ French Pat. 599,827, May 19, 1924; Brit. Chem. Abst., 1929, 300B.

²⁷ Ger. Pat. 370,974 to Chem. Fabr. Griesheim-Elektron.

identical with the product obtained by ethylation of tetrahydro- β -naphthol.²⁸ This process is not only more versatile than the catalytic method, but, presumably, demands less purification of the raw material.

4128. Non-catalytic Hydrogenation of Naphthylamine.²⁹ One process depends on the action of alkali or alkaline-earth metals and alcohols on isocyclic or heterocyclic bases in the presence of an inert solvent; the alcohol is preferably added at the same rate as it is used in the reaction. Thus tetrahydro- α -naphthylamine is formed when a solution of α -naphthylamine in alcohol is added to a mixture of solvent naphtha and sodium at a temperature above 130° C.; with a solvent of lower boiling-point, such as toluene, dihydro- α -naphthylamine is obtained. [2-Methylquinoline when hydrogenated at above 130° C. yields tetrahydro-2-methylquinoline].³⁰

4129. Other aromatic isocyclic and heterocyclic compounds, in addition to bases, can be reduced with alkali or alkaline-earth metals and alcohol in the presence of an indifferent solvent. The process is easily regulated and can be stopped at any point by withholding further addition of alcohol. Thus, tetrahydronaphthalene is obtained from naphthalene, sodium, and alcohol in the presence of solvent naphtha at 140°–150° C. [and tetrahydrodiphenyl, boiling 247°–249° C._{b10} 115°–118°, from diphenyl, sodium, alcohol, and solvent naphtha at 140°–150° C.]. Acenaphthene yields tetrahydroacenaphthene.³¹

4129A. Hydrogenation of naphthalene at high temperatures, according to Schmidt, results in a break-up of the nuclei with formation of benzene.³² Benzene and its nearest homologs are manufactured from higher homologs, polynuclear aromatic hydrocarbons, hydroaromatic and heterocyclic compounds, by bringing the compounds into intimate contact with hydrogen in the presence of a catalyst containing at least one element from the group, iron, cobalt, nickel, molybdenum, vanadium, tungsten, manganese and chromium, at a higher temperature than is required for the formation of compounds hydrogenated only in the nucleus.³³

REFERENCES ON HYDROGENATION OF NAPHTHALENE

4130. Naphthalene. von Shopnik, *Chem. Ztg.*, 1927, **51**, 211. Production of naphthalene described in detail from coal tar to purified hydrocarbon.

4131. Preparation of tetralin and decalin. Inoue, *J. Chem. Ind. (Japan)*, 1923, **26**, 1319–29.

²⁸ *Chem. Zentr.*, 1923, 539. Contrast para. 4121.

²⁹ Bayer & Co.'s Ger. Pat. 305,347, 1918.

³⁰ *Chem. Abst.*, 1919, **13**, 325. Tetrahydro-*N*-ethyl- α -naphthylamine is prepared by catalytic hydrogenation of *N*-ethyl- α -naphthylamine, in presence of nickel, at 130° C. and 30 atm. (Swiss Pat. 130,423, Apr. 8, 1927 to S. A. Ind. chim. Bâle).

³¹ Ger. Pat. 306,724 (addition to 305,347) to Bayer & Co.; *Chem. Abst.*, 1919, **13**, 611. See also paras. 2072–2085, this volume.

³² Can. Pat. 268,282, Feb. 8, 1927.

³³ *Chem. Abst.*, 1927, **21**, 1660.

HYDRONAPHTHALENES

4132. The products of the catalytic hydrogenation of naphthalene are tetrahydronaphthalene and decahydronaphthalene.³⁴ These may be obtained mixed or pure. The separation is best effected by sulphurous acid which combines with and removes the unsaturated tetrahydroderivative, the saturated decahydronaphthalene remaining unaffected.

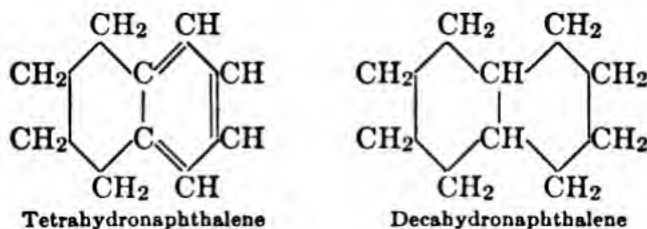
4132A. The manufacturing cost in the United States is such that commercial tetrahydronaphthalene, or tetralin, cannot be produced at a price competitive with benzol, toluol, and solvent naphtha. Tetralin is made only on a comparatively small scale in this country and doubtless could be produced at much lower cost were the demand to increase in a substantial way.

PROPERTIES OF THE HYDRONAPHTHALENES

4133. The hydronaphthalenes are water-white, pleasant-smelling, limpid liquids, and possess the following characteristics:

	Tetrahydronaphthalene "Tetralin"	Decahydronaphthalene "Decalin"
Boiling-point.	205°-207° C.	185°-187° C.
Specific gravity.	0.97-0.98	0.89-0.90
Flash-point.	78° C.	60° C.

The tetrahydro derivative, of the structural formula below is unsaturated, contains still one benzene nucleus open to substitution with halogens, nitro groups, alkyl radicals, etc. It is attacked by both sulphurous and sulphuric acid,



as well as by nitric acid in the formation of nitrotetrahydronaphthalenes. Decahydronaphthalene, on the other hand, is fully saturated and behaves exactly like a cycloparaffin, being incapable of forming substitution derivatives in the

³⁴ According to Ger. Pat. 324,861 to Tetralin Ges. m. b. H., no decahydronaphthalene is formed until the conversion to tetrahydronaphthalene is complete; *J.S.C.I.*, Apr., 1921, 253A. Using platinum sponge, Willstätter and Seitz obtained decahydronaphthalene directly. *Ber.*, 1923, **56B**, 1388; *Chem. Abst.*, 1923, **17**, 3334. See also I. G. Schroeter (with F. Stahl, H. Haehn, and C. Prigge). *Annalen*, 1922, **426**, 1-17; *J.S.C.I.*, 1922, **41**, 133A; also *Ber.*, 1921, **54**, 2963; *J. Chem. Soc.*, 1922, **121** and **122**, i, 122. See also paras. 2066-2071, this book.

way aromatic compounds do, and unattacked by mineral acids in the cold. It is therefore from tetralin that useful intermediates can be produced. Decalin is probably, however, the better general solvent and motor fuel component.³⁵

TETRALIN ³⁶

4134. Tetralin is a water-white liquid with a boiling-point of 206° C. (402.8° F.) and a specific gravity of 0.975, flash-point 80° C., freezing-point - 25° C.

4135. There are two known tetrahydronaphthalenes: one is formed by the action of phosphorus and hydriodic acid on naphthalene, this is the 1 : 4 : 5 : 8 tetrahydronaphthalene; the product obtained by the direct hydrogenation of naphthalene in the presence of a catalyst is the 1 : 2 : 3 : 4 compound.

4136. Tetralin is a very stable chemical compound even at its boiling-point. It can be sulphonated or nitrated. The sodium sulphonate has a number of interesting possibilities. Tetralin does not mix directly with water, but will readily incorporate with solutions of soap or soluble oil. Such solutions are, however, not perfect and a separation takes place after standing for some length of time. A slight agitation causes the substances to emulsify again very readily, but before a really stable emulsion of this sort can be prepared there must be some addition of hexalin or methylhexalin which will act as a homogenizing agent.

4137. Tetralin is non-poisonous, non-explosive and practically non-inflammable. Experiments conducted in Europe show that even with a considerable internal dosage of tetralin only slight toxic symptoms are observed.³⁷

4138. COMPARATIVE BOILING-POINTS EXPRESSED IN DEGREES C.

Acetone.....	56.0
Alcohol, absolute.....	78.0
Alcohol, methyl.....	60.0
Toluol.....	111.0
Spirits of turpentine.....	160.0
Benzene.....	80.4
Carbon tetrachloride.....	76.74
Pyridine.....	114.5
Tetralin.....	206.0

4139. Tetralin is a good solvent for many organic compounds including camphor, fats, oils, waxes, resins and caoutchouc. It also dissolves sulphur and picric acid. It does not dissolve shellac or the phenol-formaldehyde resins. It forms a clear solution with 3 parts of glacial acetic acid and is miscible in all proportions with alcohol, ether, petroleum ether, and chloroform.

³⁵ *Chem. Age* (London), 1922, **30**, 4, 175.

³⁶ Derived largely from material kindly communicated by Newport Chemical Works, Inc., Passaic, N. J.

³⁷ *Cf.* Para. 4158.

4140. The following table shows the solubility of ordinary beeswax in a few different solvents.

TESTS AT ROOM TEMPERATURE (22.5° C., OR 72.5° F.)

Solvents, 100 Cc.	Amount of Beeswax Dissolved, Grams	Remarks
Linseed oil	0.6	Clear.
Carbon tetrachloride	4.88	Clear.
Hydroterpine	2.92	Slightly cloudy.
Tetralin	6.8	Clear.
Hexalin	0.8	Clear.
Isopropyl alcohol	0.72	Milky.
Ethyl alcohol, C. P.	0.4	Cloudy.
Benzol, 90 per cent.	7.04	Clear.
Methyl hexalin	0.52	Cloudy.
Turpentine	1.48	Clear.

These differences in solubility preserve approximately the same ratios as the temperature is increased.

DECALIN

4141. In the hydrogenation of naphthalene into tetrahydronaphthalene 4 atoms of hydrogen are introduced, as the name implies, whereas in decahydronaphthalene there is a complete saturation with hydrogen, and the resulting compound is, therefore, not easily susceptible of chemical reactions. Decalin has a boiling-point of 188° C., a flash-point of 57° C. and a specific gravity of 0.895. Decalin, like tetralin, evaporates without leaving any residue. It possesses a somewhat higher evaporating speed than tetralin. It is a transparent liquid with a mild odor, and serves as a suitable thinner. It will not cause any discoloration even in white lacquer. On account of its high solvent power it has been suggested for use in various forms of paint and varnish removers. Decalin, like tetralin, can be brought into watery solution by the use of a small addition of hexalin soap.

4142. Derivatives of Tetralin. Tetralin as a source of intermediates for the dye and fine chemical industry merits attention. The unhydrogenated benzene nucleus reacts in a manner almost identical to that shown by benzene itself. The derivatives have been carefully examined both by the chemists of the Tetralin Company and by independent observers. Thus, Rowe has prepared many acyl tetrahydronaphthalenes²⁸ and has found them capable of use in the production of dyestuffs.

4143. The sulphonic acid of tetrahydronaphthalene is easily prepared by direct sulphonation with 100 per cent sulphuric acid at a relatively low temperature. From the 2-sulphonic acid thus produced, the corresponding naphthol can be easily obtained in the ordinary manner, fusion with caustic alkalies, and subsequent acidification. Tetrahydronaphthalene-2-naphthol is of use as a dis-

²⁸ *J. Soc. Chem. Ind.*, 1920, **14**, 241, T.

infectant. The sulphonyl chlorides are likewise easily prepared, and both the 1 and 2 derivatives can be obtained in a pure state, and the corresponding sulphonic acids, amides, anilides, thio-naphthols, etc., obtained by suitable reactions. From the thio-naphthols by a simple series of reactions involving condensation with chloroacetic acid, tetrahydrothio-naphthyl indigo can be obtained.

4144. Halogens form substitution products, just as with benzene or naphthalene.

4145. The action of nitric acid upon the hydrocarbon is of fundamental importance, and mononitro, dinitro and trinitro derivatives have been obtained. It is scarcely necessary to indicate the possibilities of development here for reduction, etc., may lead to a great number of products. Thus, amines, azo and hydrazo derivatives, hydroxyamines, benzidenes, etc., result on applying the usual reactions. The use of the hydro-naphthols or the naphthylamines in the production of azo dyestuffs is of great promise; and in short, the reactivity of the unhydrogenated part of the naphthalene structure nucleus is as yet unexplored, except for a few incursions, but these, so far as they go, have revealed a land of exploration to the dye-maker.³⁹

4146. Nitro-derivatives of Tetrahydronaphthalene. The production of these is described in Ger. Pats. 299,014 (*J.S.C.I.*, 1920, 174A), and 326,486, March 17, 1916, to Tetralin Ges. m. b. H.⁴⁰

4146A. The use of these nitro-derivatives in explosives is claimed by Schrauth.⁴¹

4147. Nitration of Decahydronaphthalene. Decahydronaphthalene is slowly converted by boiling nitric acid (*d* 1.2) into *tert.*-nitrodecahydronaphthalene, b.p. 96°–97°/2 mm., from the residue, after the fractionation of the tertiary decahydronaphthalene, crystals of dinitrodecahydronaphthalene, m.p. 164°, are obtained. The hydrochloride when boiled for twenty-four hours with potassium nitrite yields an octahydronaphthalene, b.p. 88°–89°/1.4 mm., the residue from which yields *tert.*-decahydronaphthol, m.p. 65°. α -Nitrodecahydronaphthalene, b.p. 108°–109°/14 mm., yields on oxidation α -decahydronaphthalone. [Nametkin and Madajeva-Sitscheva. *J. Russ. Phys. Chem. Soc.*, 1926, **57**, 382; *Brit. Chem. Abst.*, 1927, 234A.]

4148. Beta-tetrahydronaphthyl methyl ketone preparation from tetrahydronaphthalene, in carbon bisulphide solution, by the action of acetylchloride in presence of aluminum chloride is described by Hesse. [*Ber.*, 1920, **53B**, 1645; *J. Chem. Soc.*, 1920, **117–118**, i, 851.]

4149. Hydrogenated Anthraquinones.⁴² For the production of hydrogenated anthraquinones tetrahydronaphthalene or its derivatives are treated, when gently heated, with anhydrides of aromatic *o*-dicarboxylic acids, especially phthalic anhydride in the presence of aluminum chloride and with addition of benzene and similar diluents. The α -ketocarboxylic acids formed are changed

³⁹ *Chem. Age* (London), 1922, **30**, 176.

⁴⁰ *J.S.C.I.*, July 15, 1921, 463.

⁴¹ Ger. Pat. 300,149, Mar. 21, 1916; *J.S.C.I.*, 1921, **40**, 829A.

⁴² Ger. Pat. 346,673 to Tetralin Ges. m. b. H.

into hydrogenated anthraquinones by condensing reagents, particularly fuming sulphuric acid.⁴³

4150. Preparation of organic phosphorus compounds [from hydronaphthalenes]. Ger. Pat. 452,064, Nov. 5, 1927, to Cassella and Co.

4151. Aromatic Tetrahydronaphthylamines and Derivatives.⁴⁴ These derivatives are obtained by submitting *N*-substitution products of a naphthylamine to catalytic hydrogenation. If the derivative is an *N*-acyl-naphthylamine, the corresponding tetrahydronaphthylamine is obtained by saponifying the hydrogenation product. The individual products are directly obtained, and the process is an improvement on that in which the tetrahydronaphthalene is nitrated and then reduced, and the isomerides separated. Examples are given of the treatment of *N*-ethyl- α - or β -naphthylamine, acetyl- α - or β -naphthylamine, acetylated *N*-ethyl- α -naphthylamine, and *N*-phenyl- α -naphthylamine.⁴⁵

4152. Cyclic Ketones from Tetralin. According to Riedel⁴⁶ alpha-ketonic derivatives, useful as solvents for nitrocelluloses and as intermediates for syntheses, may be made from tetrahydronaphthalene and its derivatives by oxidation with chromic acid.

4153. Alpha-ketones from Alpha-naphthol. Alpha-naphthol and iso- or hetero-nuclear substituted alpha-naphthols, melted, or dissolved in tetralin, hydrogenated at 120°–180° C. under a pressure of 10–20 atmospheres in presence of nickel on kieselguhr yield alpha-keto-substituted naphthalenes.⁴⁷

4154. When alpha-naphthol is reduced by means of 2 molecules of hydrogen at 200° C. in the presence of nickel, the product consists of about 10 per cent of alpha-ketotetrahydronaphthalene, 25–30 per cent of *ar*-tetrahydro-alpha-naphthol and a large quantity of tetrahydronaphthalene. At low temperatures, the ketone is the main product, and it seems probable that it forms an intermediate stage in the production of the hydrocarbon. On reduction by means of sodium and alcohol in moist ether, the ketone yields *ac*-tetrahydro-alpha-naphthol. *Ac*-tetrahydro-beta-naphthol is the chief product of reduction (by the catalytic method) of beta-naphthol.⁴⁸

4155. A condensation product is made by heating [naphthalene or] a hydronaphthalene with aluminum chloride under pressure at a temperature not below 50° C. and distilling the mixture.⁴⁹

4156. Condensation products can be made between lower aliphatic acids and aromatic compounds. Among the latter are hydrogenation products of polynuclear hydrocarbons.⁵⁰

⁴³ *Chem. Abst.*, 1923, 17, 1246.

⁴⁴ Brit. Pat. 276,571, Feb. 24, 1927, to Imray (from Soc. Chem. Ind., Basle).

⁴⁵ *Chem. Age* (London), 1927, 17, 431, 311. Note para. 4128.

⁴⁶ Ger. Pat. 397,150, Nov. 20, 1920, addition to 346,948.

⁴⁷ Ger. Pat. 352,720 to Schroeter and Tetralin Ges. m. b. H.; *Chem. Abst.*, 1923, 17, 1245.

⁴⁸ G. Schroeter, with Svanoe, H. Einbeck, H. Geller and E. Riebenschm; *Annalen*, 1922, 426, 83–160; *J. Chem. Soc.*, 1922, 121, i, 127.

⁴⁹ Can. Pat. 276,270, Dec. 13, 1928, to Michel.

⁵⁰ Brit. Pat. 283,864, Jan. 17, 1927, to Chem. Fabr. Milch A.-G. (assigned to Oranienburger chem. Fabr. A.-G.).

4157. Solubility of Tetralin in Liquid Sulphur Dioxide. Fontein⁵¹ finds that the statement by Zerner and others that toluene and tetralin are not completely miscible with liquid sulphur dioxide at temperatures below 21° C. is incorrect. The clouding and deposition of crystals which may be observed are due to the presence of water in the sulphur dioxide. When the latter is dry, it is completely miscible with the substances named, at - 20° C. The tetralin used must be distilled to free it from oxidized products.

4157A. Purification of sulphonated hydronaphthalenes. Petroff, Brit. Pat. 284,859, *Illustr. Off. J.*, 1928, 849; *Pine Inst. Amer. Abst.*, 1928, 2, 5, 82.

4158. Fate of Tetrahydronaphthalene in the Organism.⁵² Tetrahydronaphthalene may be absorbed in appreciable quantities by inhalation. As a result of feeding this substance to rabbits there was isolated from the urine an optically active (dextrorotatory) compound of the composition $C_{10}H_{12}O$; evidence is adduced to show that this is probably α - β -tetrahydronaphthol; from the urine of dogs treated similarly, the only product obtained was dihydronaphthalene, and it is assumed that in this case the earlier metabolic product was α - α -tetrahydronaphthol, which substance would lose water with great ease to give dihydronaphthalene.⁵³

4159. Surface Tension of "Tetralin," "Decalin," and Lubricating Oil. The surface tensions of a lubricating oil and of decalin and tetralin have been determined by a method involving measurement of the capillary rise between two plates and by the capillary wave method. "Tetralin," d^{20}_4 0.9766, γ 3.493 mg./mm. at 18.3°. "Decalin," d^{20}_4 0.9026, γ 3.210 mg./mm. at 18.8°. Lubricating oil, d^{20}_4 0.9327, γ 3.171 mg./mm. at 19.8°.⁵⁴

4160. Formánek, for the detection and determination of tetralin in motor fuels, makes use of selective coloration by dyes as the basis of a colorimetric method.⁵⁵

4161. Application of Zelinsky's Method of Catalytic Dehydrogenation to the Detection of Decahydronaphthalenes in Low-temperature Tar.⁵⁶ Suitable fractions of low-temperature tar are freed from aromatic hydrocarbons by treatment with sulphuric acid and dehydrogenated by repeated passage at 320°-330° over platinized charcoal activated by contact with oxygen at the atmospheric temperature. The products are treated with sulphuric acid, and the sulphonic acids are decomposed into the corresponding hydrocarbons by means of superheated steam. Naphthalene, α -methylnaphthalene, and 1.6-dimethylnaphthalene are thereby isolated, thus establishing the presence of the corresponding decahydro compounds in the tar. Activated platinized charcoal is a more active catalyst than platinized asbestos.

⁵¹ *Z. angew. Chem.*, 1923, **36**, 4-6; *J.S.C.I.*, 1923, **42**, 215A.

⁵² Rockemann, *Arch. exp. Path. Pharm.*, 1922, **92**, 52; *J. Chem. Soc.*, 1922, **121** and **122**, i, 499.

⁵³ Cf. Pohl. Poisonous properties of tetralin [and hexalin]. *Kunststoffe*, 1925, **15**, from *Ztrblatt, f. Gewerbehygiene*, 1925, 91.

⁵⁴ Grunmach and Schweikert, *Z. phys. Chem.*, 1924, **113**, 432.

⁵⁵ *Chem. Ztg.*, 1928, **52**, 325, 346.

⁵⁶ Kaffer, *Ber.*, 1924, **57**, 1261-1265.

REFERENCES ON THE CHEMISTRY OF HYDRONAPHTHALENES

- 4162.** v. Auwers and Moller. Formation and spectrochemical behavior of hydrogenated naphthalene derivatives. *J. prakt. Chem.*, 1925, **109**, 124; *Chem. Abst.*, 1925, **19**, 1269.
- 4163.** v. Braun and others. Oxidative degradation of tetrahydronaphthalene and substituted tetrahydronaphthalenes to phthalonic acid and phthalic acid. *Ber.*, 1923, **56**, 2332.
- 4164.** Eisenlohr and Polenske. Stereoisomeric forms of decahydronaphthalene. *Ber.*, 1924, **57**, 1639; *J. Chem. Soc.*, 1924, **i**, 1291.
- 4165.** Hückel. Stereochemistry of decahydronaphthalenes and their derivatives. *Ann.*, 1925, **441**, 1; *Chem. Zentr.*, 1923, **iii**, 766; *Chem. Abst.*, 1924, **18**, 75.
- 4166.** Decahydronaphthalene and derivatives—stereochemistry. Hückel and others. *Ann.*, 1926, **451**, 109; also Hückel, *Ber.*, 1925, **58B**, 1449. Transformation of *cis*- to *trans*-form: dehydrogenation of decahydronaphthalene. Zelinsky and Turowa-Pollak, *Ber.*, 1925, **58**, 1292; *J.S.C.I.*, 1925, **B**, 666.
- 4167.** Stereochemistry of hydronaphthalenes. Deca-hydro-beta-naphthamides. Kay and Stuart, *J.C.S.*, 1926, 3038.
- 4168.** Decahydronaphthalene Prepared with Platinum Sponge Catalyst. Willstätter and Seitz, *Ber.*, 1924, **57B**, 683-684. An investigation of the structure of the product by refractometric methods showed that it was all *cis*-decahydronaphthalene.⁵⁷
- 4169.** Zelinsky and Gavedovskaja. Isomerization of decahydronaphthalene. *Ber.*, 1924, **57**, 2062; *Brit. Chem. Abst.*, 1925, 66B.

II. HYDROGENATION OF ANTHRACENE, PHENANTHRENE AND THEIR DERIVATIVES.

4170. Hydrogenation of Anthracene. Anthracene hydrogenated under pressure in the presence of hydrogen and a catalyst yields symmetrical octahydroanthracenes. The purified anthracene, melted, or dissolved in tetralin, is treated with hydrogen at 180°-200° C. under a pressure of 10-15 atmospheres in presence of nickel on fuller's earth.⁵⁸

4171. Purification of Crude Anthracene. Anthracene is washed with tetralin and then dissolved in cyclohexanone or cyclohexanyl acetate (or a mixture) at 90° C. On cooling anthracene crystallizes out in a state of almost chemical purity.⁵⁹

4172. Purification of Anthracene. In Portheim's method⁶⁰ anthracene and carbazole are separated by dissolving the mixture in a neutral solvent such as coal-tar naphtha and adding potassium hydroxide. The water formed during the reaction is removed by evaporation in order to prevent decomposition of the carbazole-K compound which separates as a sandy precipitate.⁶¹

4173. Hydrogenation of Anthraquinone Compounds.⁶² A German process for hydrogenation of anthraquinone and its derivatives employs heating with hydrogen in the presence of a catalyst. For production of the more highly hydrogenated compounds, an anthranol compound is used as starting material. In the case of nitro-compound amines are produced.

⁵⁷ *Chem. Abst.*, 1924, **18**, 2891. See also the same authors, *Ber.*, 1923, **56B**, 1388; *Chem. Abst.*, 1923, **17**, 3334.

⁵⁸ Ger. Pat. 352,721 to Schroeter and Tetralin Ges. m. b. H.; *Chem. Abst.*, 1923, **17**, 1245. The hydrogenation of anthracene is fully discussed by Schroeter, *Ber.*, 1924, **57B**, 2003; *Chem. Abst.*, 1925, **19**, 1271.

⁵⁹ Ger. Pat. 389,878, Feb. 2, 1922, to Tetralin Ges. m. b. H.

⁶⁰ U. S. Pat. 1,404,055, Jan. 17, 1922.

⁶¹ *Chem. Abst.*, 1922, **16**, 1099. U. S. Pat. 1,404,056, same date, to same patentee, discloses a similar method for purifying anthraquinone.

⁶² Brit. Pat. 248,759, Mar. 3, 1925, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1927, 745.

4174. Hydrogenation of Phenanthrene. Schroeter describes the product of symmetrical octahydrophenanthrenes. Purified phenanthrene, melted or in solution, is hydrogenated in the presence of catalysts. For example phenanthrene, purified by treatment with readily fusible or finely divided metals such as sodium, potassium, copper, iron or nickel, or other metallic compounds, such as sodamide or calcium carbide, is treated with hydrogen at 180°–220° at 15 atmospheres pressure in the presence of a catalyst prepared by precipitating nickel on fuller's earth. The product, b_{11} 160°–170°, is purified by way of its sulphonic acid which by treatment with hydrochloric acid gives *s*-octahydrophenanthrene. The latter compound forms crystals, melting 16.7°, b_{11} 167.5°, d_{20} 1.026. Its constitution is demonstrated in the same way as that of the *s*-octahydroanthracene (see above). *s*-Octahydrophenanthrenemonosulphonic acid gives a stable chloride which with dilute aniline solution yields a crystal anilide.⁶³

4175. Abietic Acid, which is the acid of rosin (colophony), is a phenanthrene derivative. A note on its hydrogenation will be found in paragraph 2237.

4176. Hydrogenation of Resins. The hydrogenation of various resins such as ordinary rosin, damar, sandarac, shellac, copal, pontianak, is described by Ellis.⁶⁴ Nickel, copper, cobalt, palladium, or platinum may be used as catalysts. The resin may be hydrogenated in a melted condition or in solution in an inert solvent. Petroleum or aromatic hydrocarbons may be used as the solvent material. A temperature of 180° C. is specified and a pressure of hydrogen of 10 lb. or more.

4177. Brooks⁶⁵ describes a process of manufacturing hydrogenated rosin having many of the properties of common rosin such as solubility in varnish solvents and saponifiability or soap-making properties but differing from ordinary rosin by possessing a substantial stability and diminished oxidizability as evinced by giving a lessened absorption of iodine or bromine. Varnishes can be prepared from the treated rosin which do not crack and fissure upon standing and soaps or soap compositions, sizes, etc., may be prepared from it which do not yellow with age.

4178. It is stated that ordinary rosin or colophony, although often used in the manufacture of cheap low-grade varnishes, enamels and the like, gives coatings which, in time, crack and fissure or "craze." Rosin makes an unusually lustrous varnish film, and if it were not for this lack of permanence it would be a highly desirable varnish resin. In other uses, rosin displays the same tendency to alteration and deterioration with time. Rosin soaps are not permanent but become yellower and harder on keeping. In one of the most extensive uses, sizing paper, the same tendency obtains. The lack of permanence is stated by Brooks to be largely due to the fact that rosin is an unsaturated body and, therefore, tends to oxidize when exposed to air, in the way in which it is exposed in a varnish film, in a body of soap or as the sizing in paper. In the case of rosin size in paper the oxidation not only affects the size itself but the paper as well; probably because of the development of peroxide, formic acid, etc. Rosin-sized paper, particularly if exposed to light and air, in time becomes friable and yellow. By combining or saturating the rosin with hydrogen, a material is obtained which displays all the valuable properties of rosin as regards the making of high luster varnish films

⁶³ Ger. Pat. 352,719; *Chem. Abst.*, 1923, 17, 1246. For an elaborate discussion of the hydrogenation of phenanthrene, see Schroeter, *Ber.*, 1924, 57B, 2025; *Chem. Abst.*, 1925, 19, 1274.

⁶⁴ U. S. Pat. 1,249,050, Dec. 4, 1917.

⁶⁵ U. S. Pat. 1,167,264, Jan. 4, 1916.

and the preparation of soap while it no longer has the undesirable property of lack of permanence or stability when exposed to the air. This stabilized rosin or colophony when converted into varnishes is claimed to give a high-grade varnish in lieu of the ordinary low-grade article; a varnish film which is permanent in air, and at the same time of good appearance. It is also adapted to make a better grade of soap and a higher class, more permanent paper size.

4179. Brooks observes that abietic acid, or the acid of rosin, appears to hydrogenate in stages, there being a first absorption of hydrogen which is more energetic than the later absorption. This first, easily hydrogenating stage corresponds to the highest oxidizability and if the hydrogenation be carried only to the end of this first stage the rosin loses most of its alterability in air. While the addition of hydrogen to the rosin may be performed in many ways: a simple method of procedure is to reduce the rosin to a fluid state by heat, stir in 3 per cent of freshly reduced nickel and expose the mixture to an atmosphere or current of hydrogen. Any suitable stirring or agitating means may be used to produce intimate contact of the mixture of rosin and catalyst with the hydrogen gas. A temperature of 180° to 230° C. is suitable for this operation. The progress of the reaction may be followed by watching the gauge pressure where the operation is performed under pressure. When the pressure, as indicated by the gauge, ceases to diminish with comparative rapidity, that is, the rapidity of absorption of hydrogen slackens, the first stage of saturation is over. After this time there will be a slower diminution of pressure. The treatment may be carried to a point where the iodine absorption shows no further substantial reduction on continuation of the treatment.

4180. Instead of using nickel, other metals such as cobalt, copper or iron may be employed, but these other metals are not quite as effective as the nickel. Whichever metal is used it is best reduced from an oxide formed from its nitrate, reduction being by a current of hydrogen at a low temperature; a temperature not markedly in excess of 200° C. and advantageously lower. Instead of using these metals, their oxides may be employed, but in this event it is desirable to perform the treatment with hydrogen at a somewhat higher temperature, say about 240° C. The catalyst may be used with any of the usual carriers such as kieselguhr, or asbestos, etc., to increase the contact surface.

4181. "Impregnation" with hydrogen may usually be accomplished in about three hours at 200° C., using freshly reduced nickel.

4182. In lieu of simply melting the rosin, a solvent may be used as a vehicle for the rosin and catalyst; such as alcohol or a good grade of kerosene.

4183. Instead of using the stated metals, or their oxides, colloidal palladium (or palladium chloride) or other platinum group metal, may be used. Palladium in the colloidal spongy condition is stated to be an advantageous catalyst. In using colloidal palladium, hydrogenation may be performed at the ordinary temperature or slightly higher, the rosin in this case being maintained in a fluent condition by the use of an appropriate solvent, such as alcohol, benzol, gasolene, toluene, etc. Colloidal palladium may be directly formed in or added to the rosin solution or it may be produced in an oily carrier and then added to the solution of rosin. Or a water solution of colloidal palladium may be agitated with a solution of rosin in a suitable solvent in the presence of hydrogen until the desired degree of saturation is effected.

4184. Similar results to those given by colophony may be obtained upon hydrogenation of many other resins known as varnish "gums" and in use for making varnish. It is claimed that the hydrogen treatment much improves their stability and quality. Among other resins which may be improved by hydrogenation are Pontianak and guayule resin.

4185. Brooks states that ordinarily he carries on hydrogenation till the resultant product shows an iodine value of 20 or less by the Hanus method.

4186. Hjerpested obtains a ketone-like product by destructive distillation of the calcium or barium compounds of the resins which he then hydrogenates. Distillation residues from wood tar may be treated in a like way.⁶⁶

4187. Production of Unctuous Material from Colophony. Material suitable for use in the manufacture of soap, textile preparations, etc., is obtained by the catalytic hydrogenation of a mixture of colophony and castor oil at raised temperature and pressure.⁶⁷

4188. The material obtained by hydrogenation of colophony is utilizable as and in lubricant.⁶⁸

⁶⁶ Dan. Pat. 36,064, May 31, 1926; *Chem. Abst.*, 1927, **21**, 1021; French Pat. 618,740, July 10, 1926; *Brit. Chem. Abst.*, 1928, 165B.

⁶⁷ Ger. Pat. 451,180, June 23, 1922, to A. Riebeck'sche Montanwerke A.-G.; *Brit. Chem. Abst.*, 1929, B27.

⁶⁸ Ger. Pat. 414,612, May 24, 1922, to Hugo Stinnes-Riebeck-Montan und Oelwerke A.-G.

CHAPTER XLII

USES OF HYDRONAPHTHALENES, ETC.

4200. Tetralin ¹ has found a multiplicity of uses, especially in detergents and liquid soaps. Its value in such compounds is its high solvent power over a wide range of oils, gums and waxes. Its high boiling-point is, of course, valuable in this connection, as it can be incorporated in detergents intended for use at high temperature: where tetralin is employed as the organic solvent there is no loss by evaporation at these higher temperatures. For many textile soaps and detergents it is brought into a form soluble in water by the addition of hexalin and a little soluble oil or soap.

4201. The resulting compositions have the further valuable property of reducing the surface tension of liquids which, in conjunction with the high solvent power, makes the compounds of great value for wetting out materials, causing quick penetration.

4202. We will consider a little further the properties of some of the special detergents, wetting-out compounds, aids to penetration, etc., which have as their base these hydrogenated products. What is it that makes them valuable for these various purposes? Stated briefly it is a combination of:

- a. Their solvent powers.
- b. Their property of lowering surface tension.
- c. Their property of forming emulsions with many substances.

4203. Cotton is quite resistant to thorough wetting, owing to its content of wax and oily substances, air, etc. Also the surface tension of the liquid or liquids in which the cotton is to be wetted adds a difficulty. As a factor in favor of the ready wetting out of the cotton is the force of capillary attraction and, when the wetting agent lowers the surface tension of the liquid, dissolves and emulsifies fats, waxes, oil, etc., that may be present, the full force of capillary attraction can come into play and we have the best form of wetting or penetrating agent.

4204. Owing to the high flash-point of tetralin, it can be used with greater safety as a dissolving and thinning agent in lacquers, varnishes and paints than naphtha, toluol and benzol. It finds a use in the manufacture of substances like shoe creams because the cream does not dry up as readily as with other solvents like turpentine. Some use has been made of tetralin in internal combustion engines in combination with alcohol and benzol.

¹ The information contained in paras. 4200-4207, 4235-4240 and 4300-4326 has been furnished by Newport Chemical Works, Inc., Passaic, N. J.

4205. Work has been done along the line of removing printers' ink from newspaper by a process of flotation in which tetralin-hexalin combinations are the fundamental reagents.

4206. Tetralin, because of its high boiling-point, its stability and its high dissolving powers, has been found of value as a crystallizing medium for various substances.

4207. A use of tetralin that is of growing importance is as an absorbent for casing-head gas. It absorbs from 5 to 10 per cent as against 1 to 2 per cent for straw oil, which is the absorbent generally used. The United States Bureau of Mines reports on the recovery of gasoline in the United States by the usual absorption processes, as being 70 per cent, whereas by the Brégeat process the absorption is 95 per cent. Tetralin is so active an absorbent that even the tail gases that have already been put through the straw-oil absorption process can be brought up to the 95 per cent yield figure by a further passage through the tetralin system. The gasoline so resulting has a very high purity.

4208. In this case the high boiling-point of tetralin is an advantage. In a plant for treating several million cubic feet per day the absorption system contains 30,000 gal. and the daily loss is only about 40 gal. In an absorption plant of the standard type and of the same capacity approximately four times the amount of straw oil must be used and even so with a lower recovery.

4209. Hydronaphthalenes as Solvents. Tetralin has found application as a turpentine substitute in countries where there is a favorable price differential. It seems to possess no other advantage than this local one of price.

4210. As a general solvent tetralin is handicapped by its high boiling-point, which complicates the recovery of the solvent.

HYDRONAPHTHALENES IN THE PAINT AND VARNISH INDUSTRY

4211. Marx ^{1a} describes the use of hydrogenated naphthalene as turpentine substitute, in paints, varnishes and the like.

4212. Meier discusses some of the difficulties attending the use of tetralin in paints and enamels. Slow drying, "sagging" and "curtaining" of the films and softening of the undercoats may be overcome by the use of tetralin in admixture with solvent naphthas and mineral spirits. Tetralin mixed with lime produces a glassy mass. Experiments show that films from enamels containing tetralin do not have materially less gloss than those containing other solvents.²

4213. Andes,³ discussing the use of tetralin in varnish manufacture, says that tetralin is miscible in all proportions with practically all solvents and oils used in the varnish industry, but not with by-product turpentine, with carbon disulphide or with alcohol. Its particularly good solvent action on resins and resinates of all kinds except those which are alcohol soluble, and its flash-point of 78° make it very desirable as a thinner in oil varnishes. It is not adapted for quick drying

^{1a} U. S. Pat. 1,483,739, Feb. 12, 1924, to Marx (assigned to Tetralin Ges. m. b. H.) and Brit. Pat. 156,250, Jan. 4, 1921, to Akt.-Ges. für Anilin-Fabrikation.

² *Farben Ztg.*, 1920, **25**, 2281; *Chem. Abst.*, 1920, **14**, 3805.

³ *Farben Ztg.*, 1920, **25**, 1977-1979; *Chem. Abst.*, 1920, 3162.

lacquers; a resin lacquer made with turpentine dried in five minutes while one of the same consistency made with tetralin dried in two hours, but no difference in drying time is observed in oil varnishes made with these solvents. Tetralin has slightly greater thinning properties than mineral spirits or turpentine. In spite of its high solvent powers, varnishes containing it may be used for multiple-coat work with perfect results.

4214. According to De Keghel ⁴ hydrogenation products of naphthalene, viz., tetralin, decalin, extra tetralin and tetralin spirits are superior in the manufacture of lacquers and varnishes to benzene, naphthas, polychloro derivatives of the aliphatic hydrocarbons and other turpentine substitutes. *Extra tetralin* is a mixture of tetralin and decalin, average density 0.900, b.p. 185°–195°, flash-point 60°.

4215. *Tetralin spirits* is an intermediate product, containing 40–60 per cent tetralin. The solvent power of these compounds, especially the last named, on natural and artificial resins, linnoxyn, etc., is excellent. The rate of evaporation is lower than that of turpentine. Thirty per cent resin dissolved in 70 per cent tetralin or tetralin spirits gives a varnish of good consistency, easy to spread and drying in five hours to a smooth, brilliant product. Coumaron resins in tetralin dry rapidly. Tetralin spirits, with heat, dissolves condensation products of phenols and formaldehyde. In some cases tetralin and turpentine mixtures dry unequally, giving poor varnishes. The addition of acetone or benzene remedies this difficulty. Bakelite resins give satisfactory lacquers, especially when heated to 80°–90° after applying. *Issoline*, a substitute for lacquer gum, resembling rosin, is soluble in alcohol, etc., and with oils, etc., gives an elastic product.

4216. Smith ⁵ recommends decalin as a turpentine substitute. As a solvent it is somewhat more efficient than turpentine with which it is miscible in all proportions. A mixture containing 70 per cent turpentine and 30 per cent decalin has the odor of the former. Evaporation is slower than with turpentine. The boiling-point, 190° C., makes decalin a good solvent for high-melting resins. The high flash-point, 60° C., lowers the fire risk.

4217. Vollman ⁶ points out that the high boiling-point of tetralin makes it possible with it to thin resin-oil melts in the kettle at much higher temperatures than is possible with turpentine or other turpentine substitutes; and the fire risk and loss by evaporation is very much less. The varnish coatings made from wartime linseed oil substitutes have a tendency to remain soft, and the use of pure tetralin as thinner would have a tendency to increase this fault, except that it can be used in mixtures with benzene. Tetralin extra, with its more rapid evaporation and more pleasant aromatic camphor-like odor, is to be preferred. Relative rates of evaporation of tetralin, tetralin extra and turpentine would indicate that the tetralins are entirely unsuited as thinners, but experiments show that coumaron varnishes with tetralin thinners dry much more thoroughly than the same varnishes with benzole thinners. Vollman attributes this to the fact

⁴ *Rev. chim. ind.*, 1920, **29**, 173; *Chem. Abst.*, 1920, 3803.

⁵ *Chem. Trade J.*, 1920, **67**, 253.

⁶ *Farben Ztg.*, 1919, **24**, 1689; *Chem. Abst.*, 1920, 357.

that tetralin appears to have the property of acting as an oxygen-carrier, forming peroxides which, in turn, oxidize the oils and resins in the varnish and thereby cause more rapid drying. This action is similar to that ascribed to turpentine, but the slower evaporation of the tetralin extends the oxidizing action of the thinner over a longer period than is obtained by the more rapid evaporation of turpentine. In confirmation of the oxygen-carrying properties, Vollman finds that tetralin in alkaline solution decolorizes potassium permanganate; exposed to the air, it becomes yellow and, to a certain degree, resinifies like turpentine; and when potassium iodide is added to a tetralin-water emulsion, iodine is liberated.

4218. By the use of tetralin, tetralin essence, or tetralin extra and mixtures of these with other solvents in the making of varnishes, almost any desired rate of evaporation can be obtained. The solvent action of the different grades of tetralin varies, so that they can be used in a very wide range of varnish products. Lacquers which dry by evaporation only, often have the defect that they cannot be used for second coating on account of their softening action on the first coat. This may often be overcome by the use of a relatively small portion of tetralin, which acts as solvent for the non-volatile portion of the lacquer, and then thinning the lacquer to brushing consistency with some other volatile vehicle which is miscible with the tetralin but has less solvent action on the resins, etc. Under these circumstances, the tetralin is nearly saturated with the non-volatile portion of the lacquer and therefore has very little softening effect when used for second coat work. A little turpentine mixed with tetralin easily masks the camphor-like odor of the latter.⁷

4219. Pink Discoloration of White Enamels with Tetralin. It was noticed early that white enamels prepared with tetralin as solvent soon developed a pink shade. According to Axel, Colzer, et al.,⁸ this effect is particularly noticeable on horizontal surfaces and is, apparently, due to chemical change in the condensed tetralin vapor. Any dry white enameled surface becomes similarly discolored if placed in a confined space for a few days with a few drops of tetralin.

4220. On the other hand, Gutschmidt⁹ and the others cited, claim that their experiments prove that tetralin is not the cause of the trouble. They inculcate various other constituents of the enamels. Meyenberg thinks that his experiments show that pink color is due to small quantities of sesame oil, present in the linseed oil, giving a Baudouin reaction with the furfural from the wood. Hueter attributes the discoloration to phenolic compounds present in synthetic resins, to the action of traces of iron on salicylic acid or its derivatives present in natural resins, or to zinc oxide. The Tetralin Association adds to this list of culprits or accomplices, cobalt driers and green woods. To sum up: the results are inconclusive.

⁷ Schrauth and Hueter, *Farben-Ztg.*, 1919, **25**, 535; *Chem. Abst.*, 1920, 1901. Smit Addens (*Olien en Vet en* 1920, No. 28, 353; *Chem. Abst.*, 1920, 1227) reports that 0.04 g. tetralin, on blotting paper, evaporated in ninety-three minutes, 0.04 g. tetralin extra in forty-nine minutes, 0.04 g. turpentine in fifteen minutes.

⁸ *Farben Ztg.*, 1920, **25**, 2076; *Chem. Abst.*, 1920, 3162.

⁹ *Farben Ztg.*, 1920, **25**, 2337; Hueter (*Ibid.*, 2280), the Tetralin Assoc. (*Ibid.*, 2286), and Meyenberg (*Ibid.*, 2287).

4221. The Cause of the Pink Coloration of White Enamels. According to Andes¹⁰ his experiments indicate that the pink coloration of white enamels is not specific to tetralin thinners but may also occur with turpentine; that it occurs only when manganese perborate in powder form has been ground in the vehicle along with zinc oxide, or if the vehicle contains an excess of this drier. Varnish to which manganese perborate has been added, whether by heating or in the cold, must be aged and allowed to settle, or filtered to remove all suspended particles of the drier which may not have gone into complete solution.

4222. Tetralin, a Sensitive Reagent for the Manganese Content of White-Mineral Pigments.¹¹ The pink discoloration of enamels containing tetralin thinners is ascribed by Andes to the presence of manganese driers in the form of small particles, but exhaustive tests show manganese in any form will cause a pink coloration with tetralin. Lithopone containing 0.005 per cent manganese as impurity, if moistened with tetralin, and then dried on a steam bath, shows an unmistakable pink color, which is not produced by other common paint thinners. Turpentine acts similarly, but is much less sensitive. The action is probably due to conversion of the manganese into a colloidal form of great tinctorial strength.¹²

4223. Rebs,¹³ discussing the discoloration in enamels containing tetralin, says it is very difficult to remove by heating all coloring matter derived from the seed hulls, from the linseed oil at present available (in Germany); on this account white enamels turn yellowish or pinkish. If the raw oil is clarified with 1 to 3 per cent calcium perborate, or 1 to 2 per cent zinc sulphate added at 260°, allowed to settle, and the clear oil cooked with 10 to 20 per cent tung oil, at 275°, a vehicle is produced which can be used for making white enamels perfectly free from discoloration with age, even though they contain tetralin. Objections to tetralin are its tendency to cause running and to reduce the gloss slightly, but these are overcome by using it in blends with benzol and benzine.

4224. Extensive experiments gave Meier no plausible explanation for the pink coloration of enamels containing tetralin.¹⁴

4225. Vollmann reviews the criticism of tetralin and believes that the most logical explanation of the pink coloration of white enamels containing it is that it is due to manganese. Potassium permanganate cannot exist in an enamel film, but other manganese compounds such as $\text{Mn}(\text{C}_2\text{O}_4)_2 \cdot \text{K}_2 \cdot 3\text{H}_2\text{O}$, used by Sacher for its detection, are also highly colored, and analogous compounds with zinc oxide might be formed in the films.¹⁵

4226. Tetralin as Solvent of Resins, etc.¹⁶ Tetralin can be used as a solvent for resins, fats, essential oils, liquid and solid hydrocarbons, caoutchouc, sulphur,

¹⁰ *Farben Ztg.*, 1920, **26**, 296, 356; *Chem. Abst.*, Mar., 1921, 764.

¹¹ Lauffs, *Chem. Ztg.*, 1923, **47**, 315.

¹² *Chem. Abst.*, 1923, **17**, 2511.

¹³ *Farben Ztg.*, 1920, **26**, 242; *Chem. Abst.*, 1921, 764.

¹⁴ *Farben Ztg.*, 1920, **26**, 59. See also *Farben Ztg.*, 1920, **25**, 2281; *Chem. Abst.*, 1920, **14**, 3805.

¹⁵ *Farben Ztg.*, 1920, **25**, 2386; *Chem. Abst.*, 1921, **15**, 765.

¹⁶ Ger. Pat. 320,807, Mar. 7, 1916, to Tetralin G. m. b. H.

dyestuffs and the like. The substances are dissolved in the heated tetralin or other more highly hydrogenated hydronaphthalene.¹⁷

4227. Vogel and Waltz¹⁸ make highly favorable reports on the use of tetralin in enamels, both in experimental work and in outdoor applications.

4228. Tetrahydronaphthalene in Varnish Remover.¹⁹ Ellis describes a method of making varnish remover containing wax and tetrahydronaphthalene as one of the solvents, other solvents being miscible alcoholic bodies such as benzyl alcohol, or cyclohexanol or chlorhydrin.

4229. Hydronaphthalenes, alone or mixed with other solvents such as amyl alcohol, may be used to remove dried oil colors and varnishes.²⁰

4230. Tetralin as Linoxyn Solvent. Linoxyn, which is only sparingly soluble in the usual varnish solvents, is brought into solution by heating under normal pressure with a tetrahydronaphthalene alone or together with other additions. The solution may be diluted with the usual varnish solvents. The solution dries to a sticky film which gradually becomes hard, tough, and elastic.²¹

4231. [Hydrogenated phenols and] hydronaphthalenes are used in formulae for preparing linoxyn-like substances for the manufacture of linoleum, artificial leather, etc.²²

4232. Varnish from Hydronaphthalenes.²³ By the action of an electrical discharge on tetralin or decalin, a drying varnish is obtained.

4233. An article by Gardner on tetralin, decalin and hexalin as solvents and thinners contains useful abstracts of the relevant literature.²⁴

HYDRONAPHTHALENES AS FUEL

4234. Tetralin has been used as a gasoline substitute in internal combustion motors. Thus a mixture containing 25 per cent of tetralin, 25 per cent benzene and 50 per cent alcohol (95 per cent) has been quite extensively used for automobiles in Germany. Nathan says that tetralin is equal if not superior to the usual oils for Diesel engines. Owing to its high boiling-point (205°-207°), it cannot be used undiluted as a motor fuel, but it is very suitable for the purpose when mixed with petrol, benzol, or alcohol. Tests on a Dorman bench engine indicated that mixtures of tetralin and petrol containing less than 50 per cent of tetralin are suitable for use in ordinary four-cylinder motor-car engines without any special adjustments, although not so good as gasoline alone either in flexibility of running, maximum power, or thermal efficiency. Higher compression ratios may be used with tetralin-petrol mixtures and would probably result in power

¹⁷ *J.S.C.I.*, 1920, 665A. Tetralin as a solvent for resins, rubber, etc., *Kunststoffe*, 1923, 13, 42.

¹⁸ *Farben Ztg.*, 25, 2336 (*Ibid.*, 2335).

¹⁹ U. S. Pat. 1,406,175, Feb. 14, 1922.

²⁰ Ger. Pat. 320,152, May 28, 1912, to Tetralin G. m. b. H.; *J.S.C.I.*, 1920, 665A.

²¹ Ger. Pat. 335,905, Aug. 6, 1918; *J.S.C.I.*, 1921, 40, 667A.

²² Ger. Pat. 434,318, June 19, 1924, to Consort. f. electrochem. Ind., G. m. b. H. (assignees of Deutsch and Hermann); *Brit. Chem. Abst.*, 1927, 305B.

²³ Brit. Pat. 275,813, Sept. 29, 1926, to Siemens and Halske A.-G. and Becker.

²⁴ *Paint Manufac. Assoc. of U. S.*, Circ. 1925, 248, 62.

and efficiency equal to that given by gasoline alone being obtained. On a basis of pints per boiler-horsepower hour, the 50 per cent tetralin mixture was the most economical one tried. Generally speaking, as the proportion of tetralin is increased, faults associated with incomplete combustion become more apparent.²⁵

4235. The specific heat of tetralin is 9720 calories and its high density gives it greater power per gallon than gasoline and benzol. A tank holding 26.4 gal. will contain about 160 lb. of gasoline with 798,000 calories or 189 lb. of benzol with 834,000 calories or 215 lb. of tetralin with about 950,000 calories.

4236. The flash-point of tetralin is 78-79° C., which is particularly desirable in fuel for airplanes. Pure tetralin was tested in high-compression motors and even with the highest compression did not give pre-ignition. Tetralin will not corrode metal. Samples of iron, steel, aluminum, copper bronze and brass exposed to tetralin for years showed no traces of corrosion.

4237. In the search to find a motor fuel which could be used with advantage in the usual internal combustion motor of to-day and which would stop the knocking of the engine, mixtures of tetralin with other fuels were tested. This was done very carefully at the testing station for explosion motors of the Technical University of Berlin.

4238. Mixtures of 1 part of tetralin and 1 part of gasoline (.720 and .735 specific gravity) gave the best results, also mixtures of tetralin with benzol and mixtures of tetralin, benzol and alcohol were found practical. The limits established were that 10 per cent of the total mixture should distil below 100° C. and that 30 per cent should distil below 150° C. The specific gravity of such mixtures should correspond approximately to the gravity of benzol, to avoid special adjustment of the carburetors.

4239. Practical tests of the mixtures were made on the road. A mixture of 50 per cent benzol with 25 per cent tetralin and 25 per cent alcohol was used. The motor was started as easily as with gasoline; there was no tendency to pre-ignition and no knocking was noticed even under severe testing conditions. The combustion was complete, according to analysis of the exhaust gases, and no carbon deposit was noticed on spark-plugs even after great distances had been covered. Spark-plugs which had been in gasoline engines and which showed large deposits of carbon and no longer gave good results with gasoline, were attached to the cylinders. It was observed that in a short time the fuel containing tetralin had removed the carbon from the spark-plugs. Also no accumulation of carbon occurred in the valves or other parts of the motor.

4240. The only change made to adapt the motor to the new fuel was to supply additional warm air to pre-heat the fuel mixture. The carburetors were adjusted to heavy benzol which is essential.

4241. Friesenhahn describes liquid fuel composed of hydronaphthalenes (tetra- and deca-) mixed with aliphatic hydrocarbons. This fuel is intended for use in internal combustion engines.²⁶

4242. Dietz specifies as a formula for an internal combustion engine fuel:

²⁵ Nathan, *Fuel*, 1924, 3, 346; *Brit. Chem. Abst.*, 1924, 897B.

²⁶ U. S. Pat. 1,525,578, Feb. 10, 1925.

Low-temperature tar 35 parts, ethanol or similar alcohol 35 parts, tetralin 30 parts.²⁷

4243. Tetrahydronaphthalene, with or without hydrogen, or naphthalene with an excess of hydrogen, is heated to above 400° C. in the presence of alumina with or without other metal oxides and the product is distilled to obtain the fraction boiling below 200° C. Alcohol, gasoline or other usual fuel may be added.²⁸

4244. Addition of Decalin to Benzol Fuel Mixtures. The addition to benzol, with a low toluene content, of hydronaphthalenes consisting chiefly or wholly of decahydronaphthalene, increases its energy without materially affecting the ignition point. The freezing-point of a mixture of 90 per cent of benzol and 10 per cent of decahydronaphthalene is -3° C.; a 70:30 per cent mixture freezes at -20° C.²⁹

4245. The articles named below deal with the use of hydronaphthalenes as fuels for internal combustion engines: Ostwald, the German motor fuel problem, *Brennstoff-Chem.*, 1921, **2**, 321; de Gramm, tetralin as a fuel for explosion motors, *Rev. prod. chim.*, 1921, **24**, 729; Eckart, New technical materials for explosion engines. *Illustr. Motor Ztg.*, 1922, 384; *Dinglers polytechn. J.*, **338**, 29.

HYDRONAPHTHALENES AS LUBRICANTS

4246. Lubricants from Hydronaphthalenes. Tetralin is chlorinated by means of dry chlorine in the presence of phosphorus pentachloride, and the chlor-derivative condensed with tetralin itself in the presence of phosphorus pentoxide. A good lubricating oil results on subsequent fractional distillation *in vacuo*.³⁰

4247. Decalin is given as one of the constituents of lubricants suitable for use in apparatus for condensing benzene and like hydrocarbons from gaseous mixtures.³¹

4248. Lubricant from Hydrogenated Anthracene Residues. The residue from the preparation of anthracene from anthracene oil, which is rich in phenanthrene, is dissolved in petroleum or solvent naphtha and is treated with sodium. Alcohol is then added gradually until all the sodium has been combined, the liquid is diluted with water, the aqueous solution separated, and the oil distilled. The lubricating oil is produced from the fraction boiling above 300° C. Instead of nascent hydrogen (sodium and alcohol) molecular hydrogen may be used in the presence of a catalyst.³²

²⁷ *Chem. Abst.*, 1927, **21**, 1536; U. S. Pat. 1,620,635, Mar. 15, 1927. French Pat. 646,775, 1927, to Florès, describes a motor fuel obtained by distilling products of fermentation with hydronaphthalene or other "synthetic carburant." *Chem. Abst.*, 1929, **23**, 2275.

²⁸ *Chem. Abst.*, 1927, **21**, 488; *Brit. Pat.* 246,182, Jan. 19, 1925, to J. D. Riedel A.-G.

²⁹ *Ger. Pat.* 329,833, Mar. 29, 1916; *J.S.C.I.*, Apr., 1921, 252A.

³⁰ *Chem. Age* (London), 1922, **30**, 4, 175.

³¹ *Brit. Pat.* 277,378, Sept. 13, 1926, to Ges. für Lindes Eismaschinen A.-G.

³² *Ger. Pat.* 351,201, May 15, 1917, to Schultz; *J.S.C.I.*, 1922, **41**, 539A. For the role of hydrogenated cyclic hydrocarbons in lubricants, see: Spilker, *Brennstoff-Chem.*, 1926, **7**, 261; *Z. angew. Chem.*, 1926, **39**, 997; *Chem. Abst.*, 1927, 646.

HYDRONAPHTHALENES IN THE RUBBER INDUSTRY

4249. Hydronaphthalenes are used as solvents in rubber recovery, to remove sulphur as hydrogen sulphide, the pulverized old rubber being heated under pressure with the hydrocarbon.³³

4250. Hydrocyclic Compounds in Production of Evaporation Product from Rubber Latex. The effectiveness of the protective colloids in the evaporation of latex is increased by the addition of hydrocyclic compounds such as tetra-, hexa-, methylhexa-, and decahydronaphthalene, cyclohexanol, etc.³⁴

4251. Tetralin as Reaction Retarder in Manufacture of Rubber Substitute. Rudolf³⁵ finds that, in making factice with sulphur chloride, the addition of tetralin to the vegetable oil retards the reaction and diminishes the violence. Tetralin will mix in all proportions with drying oils.

4252. Allman, Morris and Marlor³⁶ describe a composition containing rubber and cellulose esters. Rubber is dissolved in volatile hydrogenated products of aromatic hydrocarbons (cyclohexanone), etc., and is mixed with a solution of cellulose nitrate or acetate. Non-volatile hydrogenated aromatic hydrocarbon derivatives, such as *ar*-tetrahydronaphthol may be used as softening agents.³⁷

HYDRONAPHTHALENES IN DETERGENTS

4253. Hydronaphthalenes in Detergents.³⁸ A detergent is made by mixing hydrogenated naphthalene with sulphonated fat containing sulphonic acid. The mixture is neutralized and emulsified with water. The product is not affected by hardness of water.

4254. A semi-liquid, detergent emulsion contains soap, bentonite, tetralin, tetrahydro- β -naphthol, or similar hydroaromatic compound of high boiling-point.³⁹

HYDRONAPHTHALENES AS SOLVENTS

4255. Purification of Low-boiling Hydrocarbons.⁴⁰ Hydrocarbon oils of boiling-point up to about 200° C. are dissolved in hydrogenated naphthalene, preferably tetrahydronaphthalene, and subsequently separated from the solvent by distillation. Alternatively, the hydrocarbons are passed in the form of gas or

³³ Brit. Pat. 271,073, May 11, 1926, to Tengler; *Chem. Abst.*, 1928, **22**, 1706; Can. Pat. 284,014, Oct. 16, 1928; U. S. Pat. 1,660,851, Feb. 28, 1928. Yokoyama, U. S. Pat. 1,714,855, May 28, 1929, adds sodium alcoholate to the tetralin.

³⁴ Ger. Pat. 432,894, Oct. 30, 1923, to Sturchbury, assignee of Bachmann and Hebler; addition to 419,658; *Brit. Chem. Abst.*, 1927, 229B.

³⁵ *Z. angew. Chem.*, 1921, **34**, Aufstzteil, 355; *Chem. Abst.*, 1921, **15**, 3412.

³⁶ Brit. Pat. 274,968, Apr. 30, 1926.

³⁷ *Chem. Abst.*, 1928, **22**, 2292.

³⁸ Cf. paras. 4200-4203. Swiss Pat. 119,114 (addition to 111,767), Mar. 23, 1926, to G. Zimmerli Chem-tech. Fabr.

³⁹ U. S. Pat. 1,544,588, July 7, 1925, to Moseley.

⁴⁰ J. D. Riedel A.-G., Ger. Pat. 430,974, May 15, 1926.

vapor through a quantity of hydrogenated naphthalene maintained above the boiling-point of the hydrocarbons.⁴¹

4256. Extraction of Oil Shales and Lignites with Tetralin.⁴² Tetralin under pressure (e.g., 14 atmospheres) and at a temperature of 200°–270° C. extracts more from oil shales and lignites than does benzene under similar conditions.

4256A. Novak and Trebicky use hydronaphthalenes to extract coal, peat, shale, etc., at 400°–440° C. under 20 atmospheres pressure. The products are neutral oils, montan wax, phenols, bitumen.⁴⁴

4257. Hydronaphthalenes may be employed, by themselves or in combination with other substances, for the purpose of keeping in solution, by their mere presence in the tar oils, the naphthalene which, usually mixed with anthracenes, separates out from the tar oils when stored for some length of time, forming residues difficult to work up. The cleaning of the containers may be dispensed with, while, on the other hand, it becomes possible to recover the anthracene free from naphthalenes, in the form of a crystalline mass, which may easily be pressed off. Finally, the loss of the naphthalene, useful for heating and preserving purposes, is obviated.⁴⁵

4258. Tetralin can be advantageously used for recovering sulphur from active charcoal used for gas purification. Schreiber⁴⁶ points out the ease of recovery of both the sulphur and the solvent, which in view of the relatively high price of tetralin is important. Tetralin does not affect the activity of the charcoal and, therefore, the extraction can be carried out in the purification chamber itself.

4259. Tetralin—Use in Gas Washing.⁴⁷ Tetralin is better than decalin, hexalin and methylhexalin for removal of naphthalene from coal gas.

4260. Brégeat uses tetralin, decalin, hydrogenated cresols, hydrogenated terpenes or other hydroaromatic compounds to remove from gases tar, naphthalene, paraffin, etc., which obstruct pipes. The gas is treated with these products and their presence in the gas causes removal of naphthalene already deposited.⁴⁸

MISCELLANEOUS USES OF HYDRONAPHTHALENES

4261. For the purpose of lubricating threads and fibers a mixture is used composed of a neutral petroleum oil with a wetting agent. Suitable wetting liquids are decalin or hydrogenated cresol.⁴⁹

4262. Hydrogenated naphthalenes and hydrogenated phenol are among the

⁴¹ *Brit. Chem. Abst.*, 1926, 864B. Cf., para. 4207.

⁴² Berl and Schmid, *Brennstoff-Chem.*, 1926, 7, 149, 181; cf. Ger. Pat. 411,540, May 7, 1922, to Berl. Berl and Schildwächter, *Brennstoff-Chem.*, 1928, 9, 105.

⁴³ *Brit. Chem. Abst.*, 1926, 652B.

⁴⁴ *Brit. Pat.* 234,564, Mar. 6, 1924.

⁴⁵ Ger. Pat. 301,651, Apr. 23, 1916, to Tetralin G. m. b. H.; *Chem. Abst.*, 1921, 1986.

⁴⁶ *Brennstoff-Chem.*, 1926, 3, 355; Cf., Jaeger, *ibid.*, 356; *Chem. Abst.*, 1923, 17, 2183.

⁴⁷ Weissenberger, *Glückauf*, 1925, 61, 426. Weissenberger and Schuster, *Z. angew. Chem.*, 1925, 38, 626.

⁴⁸ *Brit. Pat.* 296,925, Nov. 24, 1927. Removal of benzene [from coal gas] by means of tetralin is discussed by Sellie, *J. éssines gaz.*, 1927, 51, 267.

⁴⁹ *Brit. Pat.* 277,649, Sept. 16, 1927, to Zimmerli.

liquids used to protect cellulose acetate in mixed textiles during mercerization of the cotton fibers.⁵⁰

4263. Viscose filaments are given a matt finish by adding, to the spinning solution, 5 per cent on the weight of cellulose of various compounds, e.g., tetralin.⁵¹

4264. Coagulating Bath for Viscose. Sulphonic acids of hydronaphthalenes are among the constituents of a coagulating bath for viscose threads.⁵²

4265. Tetralin is used in bleaching of fabrics and yarn.⁵³

4266. Hydronaphthalene as an Illuminant. Wimmer⁵⁴ proposes to use hydronaphthalenes, alone or mixed with other illuminants, in an ordinary coal-oil lamp and states that this gives a flame of high luminosity.

4267. Hydronaphthalene as Smudge-producers. Van der Linden proposes to form a fuel for producing smudge fires (to protect plants from frost) by impregnating peat litter with suitable liquids: among the latter he names the hydronaphthalenes.⁵⁵

4268. Hydronaphthalenes and Hydrophenols as Preventers of Evaporation Loss. Brégeat claims that the addition of hydronaphthalene or hydrophenol (2-4 per cent) to highly volatile hydrocarbons, such as petroleum ether and ligroin, reduces evaporation losses.⁵⁶

4269. Tetralin and Derivatives as Germicides (disinfectants). Lockemann and Ulrich⁵⁷ affirms that tetrahydronaphthols are stronger germicides than the corresponding naphthols and the sodium tetralinsulphonate and octahydroanthracene sulphonate than the corresponding hydronaphthalene and hydroanthracene compounds.

4270. Chlorotetralin as Insecticide. An insecticide comprising chlorotetrahydronaphthalene is prepared by treating naphthalene with chlorine in presence of ferric chloride.⁵⁸

4271. Hydronaphthalenes are among the substances which may be used as solvents for the coloring matter of inks for printing on celluloid, synthetic resins, rubber, etc.⁵⁹

4272. Viscous Oils from Hydronaphthalenes.⁶⁰ Viscous oils which can be readily sulphonated to yield water-soluble products are prepared by treating hydrogenated naphthalenes with alkyl halides or acid chlorides with or without the addition of condensing agents. Tetrahydronaphthalene forms with benzyl chloride and zinc chloride at 120° C. an oil with boiling-point 200°-202° C. (20

⁵⁰ Brit. Pat., 273,830, Apr. 12, 1926, to Calico Printer's Association Ltd, et al.; *Chem. Abst.*, 1928, **22**, 2068.

⁵¹ Brit. Pat. 273,647, Nov. 27, 1926, to Borzykowski, assignor to Borvisk Synd., Ltd.

⁵² Brit. Pat. 234,188, Feb. 25, 1924, to Kämpf; *Chem. Abst.*, 1926, 830.

⁵³ Ger. Pat. 388,925, Aug. 2, 1922, to Mohr and others.

⁵⁴ Ger. Pat. 302,488, July 23, 1915; *J.S.C.I.*, 1921, 253A.

⁵⁵ Brit. Pat. 157,448, Jan. 10, 1921; *Chem. Abst.*, 1921, 1985.

⁵⁶ Brit. Pat. 230,311, May 9, 1924, to Page (from Brégeat).

⁵⁷ *Desinfektion*, 1924, **2**, 1; *Chem. Zentr.*, 1924, **95**, I, 1811; Ger. Pat. 324,757, July 11, 1919; *J.S.C.I.*, 1920, 831A.

⁵⁸ Brit. Pat. 203,904, Sept. 14, 1922; *Chem. Abst.*, 1924, 728.

⁵⁹ Brit. Pat. 296,461, May 3, 1927; *Chem. Abst.*, 1929, **23**, 2541.

⁶⁰ Tetralin, Ges. m. b. H.; *J.S.C.I.*, 1920, 623A; Ger. Pat. 319,799, Dec. 4, 1917.

mm.), and viscosity 3.2° (Engler) at 50° C.; with chlorinated xylol, an oil of viscosity 5°–6° (Engler) at 20° C.; with benzoyl chloride and a little phosphorus pentoxide at 280°–300° C., an oil with boiling-point 228°–230°, and with chlorinated tetrahydronaphthalene and a little phosphorus pentoxide, an oil with boiling-point (15 mm.) 240°–243° C., viscosity 35.5° (Engler) at 50° C., sp. gr. (15° C.) 1.104, and flash-point about 200° C. From decahydronaphthalene, benzyl chloride, and a little phosphorus pentoxide, at 170°–190° C., a very viscous, dark green oil is obtained.

4273. Condensation Products. Tetralin is one of the hydrocarbons mentioned by Michel⁶⁰ as forming condensation products with olefines (such as ethylene) in the presence of aluminum chloride (or other catalytic halide), at temperatures of 100°–200° C. under increased pressure. The oily products may be used as motor fuels or as intermediates.⁶¹

4274. Resinous Condensation Products (from Hydrogenated Naphthalene).⁶² Hydrogenated naphthalene is treated with formaldehyde in the presence of acids, with or without the addition of a solvent or diluent. The products can be worked up with turpentine and linseed oil for the manufacture of varnishes.⁶³

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⁶⁰ U. S. Pat. 1,667,214, Apr. 24, 1928.

⁶¹ *Chem. Abst.*, 1928, **22**, 1980.

⁶² A.-G. für Anilin-Fabr., Ger. Pat. 305,575, Apr. 19, 1917; *J.S.C.I.*, June, 1921, 439A.

⁶³ Hydroaromatic Bodies Used in Preparation of Synthetic Resins. *Brit. Pat.* 276, 518, Oct. 4, 1926, to Johnson (from I. G. Farbenind., A.-G.).

⁶⁴ *Chem. Abst.*, 1923, **17**, 3796.

⁶⁴ *Chem. Abst.*, 1924, **18**, 2568.

tion of tetralin and decalin from naphthalene; the production of isoprene from acetylene and sodium acetone; the oxidation of paraffin to fatty acids; new methods for refining petroleum oils, etc.⁶⁵

4283. Lüdecke. Shoe pastes. *Seifen. Ztg.*, 1920, **47**, 815; *Chem. Abst.*, 1921, **15**, 766. Arguing for tetralin instead of turpentine in shoe pastes.

4284. Mailhe. Hydrides of naphthalene. *J. usines à gaz.*, 1922, **46**, 30-36. Their preparation by catalytic means, their properties and their commercial application as tetralin are discussed.⁶⁶

4285. Mezger and Egger. A severe benzine and tetralin explosion. *Chem. Ztg.*, 1923, **47**, 381. Crude-oil tank was being scrubbed out with mixture of benzine and tetralin. An electric short circuit on the lamp used caused an explosion. One man was killed by burns and two by carbon monoxide poisoning.

4286. Schoon. Tetralin in shoe-creams and floor waxes. *Seifen. Ztg.*, 1920, **47**, 937; *Chem. Abst.*, 1921, **15**, 955. Practical: with recipes.

4287. Schrauth. Technical production and application of hydrogenated organic compounds. *Z. angew. Chem.*, 1922, **35**, 25; *Chem. Abst.*, 1922, **16**, 1422. Among products described are tetralin, hexalin (cyclohexanol), and cyclohexene (tetrahydrobenzene). By development of hydrogenation industries Germany may gain a position in international chemical trade which may compensate for the loss of her dominance in coal-tar products.

4288. Schroeter. Tetralin. *Kunststoffe*, 1921, 23 (from *Umschau*, 1921, 213).

4289. Utz. Hydronaphthalenes in the rubber industry. *Gummi-Ztg.*, 1920, **37**, 779; *Chem. Abst.*, 1920, 3002.

4290. Schroeter, Müller and Huang, Hydrogenation of Phenanthrene, *Ber.*, 1929, **62B** 645; *Brit. Chem. Abst.*, 1929, 548A.

4291. Killheffer. New solvents made by the hydrogenation process. *Amer. Dyestuff Reporter*, May 11, 1926.

⁶⁵ *Chem. Abst.*, 1921, **15**, 4006.

⁶⁶ *Idem*, Naphthalene. *Ibid.*, 1921, **45**.

CHAPTER XLIII

CYCLOHEXANOL, CYCLOHEXANONE, ETC.

HEXALIN¹

4300. Hexalin is cyclohexanol or hexahydrophenol, and is produced by the hydrogenation of pure phenol. It is a neutral water-white liquid and, like all higher alcohols, does not dissolve readily in water. It has a specific gravity of 0.945 (7.9 lb. to the gallon) and boils at 155° to 160° C. Its flash-point lies at about 68° C. It will not decolorize on standing, is very stable even at the boiling-point and evaporates without leaving a residue. Hexalin has a high solvent power for solid and liquid hydrocarbons, fats, oils, resins, waxes and the like.

4301. Hexalin Solvent for Resins, Synthetic and Natural. The high dissolving power of hexalin is of importance. For instance, it has been found that hexalin mixed with decalin is an excellent solvent for resins and, in particular, easily dissolves a considerable range of the condensation products of phenol and formaldehyde, which are not soluble at all, or not easily soluble in most solvents. In fact, solutions of these synthetic resins in a hexalin-decalin medium have been prepared which remain clear when diluted with non-solvents. The solution obtained is suitable for lacquering wood and other substances, it does not dry any more slowly than turpentine lacquers, and it leaves the resin in the form of a clear coating hard to remove from the foundation.

4302. For solution of synthetic resins, other combinations of these solvents can be employed as, for instance, hexalin can be substituted by its ester, hexalin acetate and the decalin can be substituted by tetralin. Hexalin has also a high solvent power for gums and other products used in the varnish and lacquer industry.

4303. Linoxyn Solutions. Linoxyn has been used to a great extent in the manufacture of linoleum, but its application in the lacquer industry has been restricted because of the difficulty of finding a suitable solvent. It is true that linoxyn is soluble in amyl alcohol and amyl acetate, but such solutions require a long period for their preparation and clarification. It has been found that clear, transparent and non-depositing solutions, which can be further thinned with other lacquer solvents, can be obtained by the use of cyclohexanol or cyclohexanone. The solutions obtained dry to an initially sticky, but eventually tough and elastic film. The drying can be accelerated by the addition of siccatives.

¹ The information in paras. 4300-4326 is largely furnished by the Newport Chemical Works.

Linnoxyn solutions are serviceable not only in the lacquer and varnish industry, but also in the manufacture of linoleum, artificial leather, etc.

4304. Rubber Dissolving Agent. Cyclohexanol or some of its conversion products are capable of dissolving both crude and vulcanized rubber. Crude rubber can be wholly or partly dissolved with well-known volatile solvents such as benzine, benzol, carbon tetrachloride, etc., and vulcanized rubber with xylene, aniline, etc., in order to subject it to further treatment after removing the foreign ingredients and eliminating the solvents. In a number of solvents the rubber swells up well, but is only partly dissolved. Large quantities of the solvent are consequently required which afterwards have to be recovered. On the other hand, some of the solvents have the disadvantage that their solvent power is exerted only at relatively high temperatures.

4305. It has been found that cyclohexanol and its esters, as well as cyclohexanone, exercise a solvent action both quickly and perfectly and at lower temperature than is the case with most other solvents. Even where high temperature is used the high boiling-point of the cyclohexanol and the reduced fire risk afford great advantages.^{1a}

4306. Mixing of Celluloid and Rubber. It is well known that the one difficulty of making a mixture of celluloid and rubber is in the finding of a solvent in which rubber and celluloid are simultaneously soluble. A number of the most common solvents of celluloid, such as acetone and amyl acetate, precipitate rubber from its solution, while celluloid is entirely insoluble in most rubber solvents, such as carbon tetrachloride, carbon disulphide, etc.

4307. A solution of celluloid and rubber made by dissolving each material separately in hexalin and then admixing the two solutions has been used to prepare a composite film of celluloid and rubber. Methyl hexalin can be employed in a similar way.

4308. Homogeneous Liquid Mixtures. Hexalin is valuable as a homogenizer when added to certain other solvents which by themselves are not miscible either with each other or with water. Also there are certain solvents which are miscible with water in some proportions, but separate on great dilution. Other solvents will mix with each other, but are not clear. As an instance of this, mixtures of 50 parts of tetralin and 50 parts of spirit, form milky solutions, whereas by the addition of 5 parts of cyclohexanol these are converted into clear solutions. Methyl cyclohexanol and cyclohexanone share these properties.

4309. Tetralin is not directly miscible with water, but if the tetralin is incorporated with some soluble oil, or soap, and a small percentage of cyclohexanol added, the resulting mixture can be considerably diluted with water without separation of the solvents.

4310. A striking example of the effectiveness of hexalin is in the case of tetrahydronaphthalene-sulphonic-acid sodium salt, which is only slightly soluble in water. If 35 parts of this salt and 65 parts of water are taken the sodium salt will not dissolve. Hexalin is not itself miscible with water, yet if to the above, 50 parts of hexalin are added the whole at once goes into a perfect solution and

^{1a} But see para. 4339.

this solution is capable of dilution with large quantities of water without any separation of the components.

4311. Emulsifying Agents. The high dissolving capacity of hexalin and methyl hexalin and their ability to form with watery soap solutions perfectly clear solutions which, in turn, possess high emulsifying properties, have led to their use in the preparation of spinning oils, loom oils, etc., which are readily washed out with water.

4312. It has been found that cyclohexanol, which, as stated, is itself insoluble in water, can be easily incorporated in an ordinary soap body and that this, dissolved in water, gives clear dilutions which even under ordinary temperature conditions possess a high dissolving and emulsifying property for neutral fats, waxes, fatty acids, solid and liquid hydrocarbons. These cyclohexanol-soap mixtures can be used either solid, semi-solid or liquid wherever the removal of fatty substances is involved as, for instance, in the textile or leather industries; and they afford excellent emulsifiers for all substances which cannot be easily, if at all, affected by watery solutions.

4313. Hexalin and Methyl Hexalin in Soap. Hexalin has a not unpleasant odor and one which is suggestive of phenol and slightly of menthol. Methyl hexalin perhaps has the menthol odor developed a little more strongly than hexalin. Hexalin is not changed by storing or slow evaporation, that is to say, it does not turn dark as does phenol. It retains its water-white oily character and is, in general appearance, quite suggestive of gasoline. As far as the use in soap is concerned the remarks made for hexalin are applicable to methyl hexalin.

4314. These are both used now quite extensively in the manufacture of soaps, liquid detergents and special emulsifying compounds. Their use in soap imparts valuable properties of solubility and emulsification and, of course, their high boiling-point prevents a material loss of the solvent ingredients when the soap is used at high temperature.

4315. The use of soaps prepared in this way is not confined to the textile industry, but extends to the laundry and general household field because of the easy removal of dirt, fat, oil and even bloodstains. In the presence of hexalin, it is claimed, blood loses the capacity to coagulate.

4316. A point of interest is that where hexalin is incorporated in a soap, other solvents such as tetralin, benzol, carbon tetrachloride and turpentine can be incorporated also, if desired, and the resulting soap compositions will appear homogeneous and will remain soluble in water even on great dilution.

4317. The peculiar odor of hexalin is not disagreeable during the washing process and the vapor is claimed to have no harmful effect on the workmen. It is also of importance to know that this odor does not adhere to the material after rinsing.

4318. Hexalin in soaps will also dissolve such water insoluble substances as magnesium and lime soaps. If hard water is used the disagreeable feature of sticky precipitates of lime soaps is said to be eliminated. Small additions of hexalin do not affect the foaming of the soap: larger additions, however, do act in the same way as equally large additions of other alcohols.

4319. The presence of hexalin in neutral water-soluble soaps has the effect of retarding the hydrolysis of the soap even when solutions of the latter are considerably diluted.

4320. In the manufacture of solid soap hexalin should not be added in its pure form to the hard soap mass. It should be admixed with a watery potash or soda soap. However, it is important that the solutions be quite hot when incorporated, and they must be stirred thoroughly to get a uniform distribution of the hexalin. The manufacture of hexalin and methyl hexalin soaps is described in a paper published in *The American Dyestuff Reporter*, May 31, 1926.

4321. Hexalin in Lacquer. Hexalin, although an alcohol, is a solvent for nitrocellulose but, on account of its high boiling-point and its somewhat slow action on the cotton, is not recommended as the sole solvent; it should be used in conjunction with lower boiling solvents. It is also a solvent for various types of resins used in the lacquer industry. Hexalin not only prevents blushing under the most severe conditions, but also produces a better flow in the application of the lacquer and a film free from orange peel.

4322. It has been found that on adding approximately 10 per cent of hexalin the viscosity of the lacquer is greatly reduced. Various resins or nitrocellulose dissolved in hexalin can be thinned to a great extent with non-solvents without precipitation.

4323. Cyclohexanol has been found available in connection with the preservation of wood because, when converted into a watery solution or emulsion, it acts as a carrier for other substances. It has also a fungicidal effect. Its powers of reducing surface tension and, therefore, inducing ready and quick penetration enables it to carry various materials very thoroughly into and through the products being treated. Experiments have been conducted by several experiment stations in different parts of the country to determine the extent of the fungicidal and germicidal value of hexalin in connection with plant life.

METHYL HEXALIN

4324. This is sometimes also called heptalin. Methyl hexalin is a mixture of the three isomeric methyl cyclohexanols obtained by the hydrogenation of cresol. During the process of hydrogenation the acid character is lost entirely, the resulting product is completely neutral and the odor is also entirely changed; in fact, instead of being rather disagreeable, the odor somewhat suggests camphor or menthol, and does not change either in long storing or by slow evaporation. Methyl hexalin boils between 160° and 180° C. Its specific gravity is .93 at 15° C. and the flash-point is about 68° C. The dissolving capacity of methyl hexalin for fats, oils, waxes, resins, etc., is about the same as that of hexalin.

4325. The greatest use of methyl hexalin is in connection with the manufacture of soaps and other detergent compounds. As in the case of most monohydric alcohols of high molecular weight the solubility of hexalin and methyl hexalin in water is very slight, in fact, almost *nil*, whereas watery soap solutions are capable of absorbing large quantities of these solvents. Olein potash soap

with a content of about 25 per cent of water dissolves any desired quantity of hexalin or methyl hexalin, and soap solutions with as little as 5 per cent soap content still absorb hexalin to the extent of many times the quantity of soap present. For methyl hexalin the solubility in watery soap solutions is somewhat less, but nevertheless in most cases well in excess of double the soap content. Methyl hexalin, like hexalin, dissolves magnesium and lime soaps and this dissolving capacity is not lost in a watery soap solution so that such a preparation, used where hard water conditions prevail, is useful.

HEXALIN ACETATE

4326. This is a colorless liquid with a typical ester-like odor. It is made by the esterification of cyclohexanol. It has a boiling-point of 175° to 185° C., specific gravity .95. It is non-miscible with water and distils without decomposition. Hexalin acetate is a good solvent for soft and hard natural resins and gums (including hard copals) shellac, nitrocellulose, celluloid, crude rubber, fats, oils (fixed, mineral and essential), and waxes. Hexalin acetate is similar in its properties and actions to butyl acetate and amyl acetate, but has, of course, a higher boiling-point. This ester of hexalin has not, up to the present time, found nearly as large a use as the alcohol, hexalin itself.

COMMERCIAL CYCLOHEXANONE ¹

4327. Cyclohexanone is a colorless liquid, with a smell resembling that of acetone. Boiling-point 155°–160° C.; density 0.95; flash-point 150° F. (66° C.) This anhydrous solvent distils without decomposition and may be steam distilled quantitatively from various mixtures. It is non-inflammable, non-explosive, and commonly considered to be non-toxic. It does not attack metals.

Cyclohexanone is used in varnish, paint, enamel, polish, aviation dope, celluloid, film, artificial leather, linoleum, rubber, waterproofing industries, etc. In cellulose ester lacquers cyclohexanone is used as a solvent of the "medium boiler" type, assisting the flow of the lacquer over the surface and also preventing "blushing" or "chilling." Owing to the comparatively low volatility of cyclohexanone, cellulose ester lacquers made with this solvent can be brushed well. As cyclohexanone has a high flash-point it has a great advantage in this respect over many of the solvents commonly used in these lacquers. Nitrocellulose and celluloid are very readily soluble in cyclohexanone, giving perfectly clear solutions. Cyclohexanone is miscible in all proportions with butyl acetate, acetone, alcohol, white spirit, and turpentine. It is a solvent for colophony, ester gum and shellac. It is one of the few good solvents for hard copal resins, e.g., pale kauri, brown kauri, and congo copal, and is a better solvent for these hard resins than acetone, ether, turpentine, and tetrachlorethane. Solutions of these resins readily permit the addition in the cold of several times their volume of boiled

¹ Sometimes designated by the trade name "Sextone."

linseed oil. Synthetic resins of the phenol-formaldehyde type are soluble in cyclohexanone if they have not been polymerized too far.

4328. Crude rubber dissolves completely in cyclohexanone on heating for a few hours at 60°–70° C.; 20 per cent solutions of plantation crêpe, medium quality wild rubber, and best quality wild rubber are easily obtained under these conditions. A 10 per cent solution of plantation crêpe is perfectly clear and has a viscosity no greater than that of an average sample of glycerol. A 10 per cent solution of medium quality wild rubber in this solvent has a remarkably low viscosity. Ten per cent and 20 per cent solutions of plantation crêpe, medium quality wild rubber, and best quality wild rubber give firm and adhesive films when dried on glass plates.

4329. Cyclohexanone is a good solvent for fats, oils (fixed, mineral, and essential), and waxes.³

4330. Cyclohexanol, Cyclohexanone, etc.⁴ Aromatic hydrocarbons, other than naphthalene or their substitution products, are hydrogenated by treatment with hydrogen in the presence of catalysts consisting of mixtures of nickelic oxide and cupric oxide, with or without the addition of manganic oxide. The material may be hydrogenated in either the liquid or gaseous state, and under ordinary or increased pressure. Examples are given of the production of cyclohexanol, a mixture of cyclohexanol and cyclohexanone, hexahydrotoluene, and hexahydroxylene, by hydrogenating respectively phenol at 140°–150° in the presence of nickelic oxide and cupric oxide, phenol at 170°–180° in the presence of nickelic oxide, cupric oxide, and manganic oxide, toluene at 160°–200° in the presence of nickelic oxide and cupric oxide, and xylene at 180°–200° under 15–30 atmospheres pressure in the presence of manganic oxide, cupric oxide and nickelic oxide precipitated on kieselguhr.

4331. Determination of Hydrogenated Phenols, in Presence of Hydro-naphthalenes. Determination of Methylhexalin in Presence of Tetralin.⁵ A method for determining methylhexalin in the presence of tetralin depends on the distribution of the former between the latter and water. If y be the amount of methylhexalin found in the water layer when 15 g. of a mixture of methylhexalin and tetralin are shaken with 300 g. of water, then x , the percentage content of methylhexalin in the mixture is given by the equation $y^{1.3} = 0.76x$. In practice the mixture is obtained free from impurities by steam distillation, the methylhexalin in the aqueous layer being extracted with ether and recovered, while that in the tetralin layer is shaken out with water and determined as above.⁶

4332. Hydrohexalin (in the Manufacture of Soaps and Water-soluble Oils).⁷ A water-soluble preparation of methylhexalin is commercially known as hydro-

³ The information in paras. 4327–4329 is obtained from matter furnished by Messrs. Howards and Sons, Ltd., and refers to their product "Sextone."

⁴ Ger. Pat. 383,540, Mar. 24, 1918 (addition to 298,541), to A.-G. für Anilin-Fabr., assignees of Marx and Mombert. *J.S.C.I.*, 1924, 578B.

⁵ Lindner and Zickermann, *Chem. Umschau.*, 1927, 34, 199; *Brit. Chem. Abst.*, 1927, 713B.

⁶ James. Determination [and detection] of hexalin and methylhexalin in soaps. *Seifen. Ztg.*, 1924, 51, 859, 877; *Chem. Abst.*, 1925, 19, 742. The abstract is full.

⁷ Arndt, *Kunststoffe*, 1921, 17, 4–5.

hexalin (hydralin). This may replace Turkey red oil as general solvent and emulsifier for fats, and should further simplify the manufacture of water-soluble oils. The solvent power of hydralin is equal to that of methylhexalin, but while methylhexalin is soluble only in aqueous soap solutions, hydralin will dissolve clearly in any proportion in water and stay continuously in solution even at a high dilution. Hydrocarbons, such as gasoline, benzene, kerosene, tetralin, decalin, euterpin, oil of turpentine, and carbon tetrachloride, will, when dissolved in hydralin, form stable emulsions with water. With the use of these in the manufacture of hard and fluid soaps, products with good cleaning effects may be obtained. A number of water-soluble disinfectants with carbolic acid and cresol have been prepared from hydralin, but the latter alone, it is claimed, has disinfecting power.⁸

4333. The Use of Hexalin and Methylhexalin for Soap Making.⁹ Experiments are recorded by Bergo in which 7.5 per cent methylhexalin were mixed with a charge of 50 tallow and 50 palm-kernel oil acids and the mixture was run into 50 parts of 39° caustic lye. Saponification occurred rapidly and then 5, 10, 15 and 20 per cent of hydrocarbon oil (decalin) were added to small trial portions of the charge and, for comparison, the same tests were made using benzine, carbon tetrachloride, trichloroethylene, and tetralin. Those soaps which contained 5 and 10 per cent hydrocarbon oil were normal in consistency; those with 15 and 20 per cent were slightly softer, and normal after air drying. All showed a good lather and possessed notable cleansing power. The odor of the decalin soaps was far better than that of the others. Bergo suggests that the textile industry is the proper field for such soaps, especially for the liquid potassium soaps. Two such liquid potassium soaps were made, one with 100 parts methylhexalin and 100 parts soya-bean acids, the other with 100 methylhexalin and 100 palm-kernel oil acids. After a rapid saponification 50–100 per cent of methylhexalin, benzine, tetralin, etc., were added as before to small test portions. Some of these diluents thickened the soap in the smaller additions but thinned it again in the larger proportions. The finished soaps were clear liquids up to 200 per cent additions, but turbid above 200 per cent. When diluted with 10 volumes water, the soaps below 200 per cent gave clear solutions, those above 200 per cent produced permanent emulsions. The cleansing power of these methylhexalin soaps is good.¹⁰

4334. Bergo¹¹ recommends the use of hexalin and methylhexalin for soft soaps (potassium soaps) and liquid soaps. As much as 20 per cent methylhexalin produces soaps of excellent cleansing power.¹²

4335. Cheap Soaps and Economy in Washing Compounds.¹³ An outline of small-scale preparation of heavily filled cold-made soaps, with a recommendation to introduce liquid soaps containing hexalin or methylhexalin, which increase

⁸ *Chem. Abst.*, 1927, **21**, 1367.

⁹ Bergo, *Seifen. Ztg.*, 1922, **49**, 416–7.

¹⁰ *Chem. Abst.*, **16**, 1922, 2789.

¹¹ *Seifen. Ztg.*, 1922, 361.

¹² *Chem. Abst.*, 1922, **16**, 2619.

¹³ Spangenberg, *Z. deut. Oel Fett-Ind.*, 1923, **43**, 274–275.

their cleansing power beyond that of the best laundry soap is given in an article by Spangenburg.¹⁴

4336. While Schrauth¹⁵ says that hexalin or methylhexalin when present to the extent of 20–30 per cent in soap prevents the formation of lime soap precipitates in hard water, Löffl¹⁶ says that this is true only of strong solutions. The solutions used in laundries are too weak.

4337. Friesenhahn compounds ordinary soap with a mixture of higher alcohols (e.g., cyclohexanol) and aromatic or hydroaromatic sulphonic acids (e.g., naphthalene sulphonic acid or hydronaphthalene sulphonic acid) or their sodium salts.¹⁷

4338. Welwart¹⁸ describes the manufacture of hexalin, etc., and discusses the properties of hexalin and methylhexalin. He says that the addition of these substances, in small quantities, greatly enhances the detergent power of soaps.

4339. Experiments on Mixtures Containing Rubber, Celluloid and Hexalin. Jones¹⁹ reports that rubber and celluloid are insoluble in hexalin. Solutions of celluloid in amyl acetate and of rubber in benzine were, however, compatible with 20 per cent of hexalin (in total volume) added to the solutions. Very slow-drying varnishes were formed which had a brilliant gloss.

4340. Hay²⁰ uses hexanol (*inter alia*) for stabilizing bituminous emulsions.

4341. Cyclohexanone is one of the agents used in a process for relustering dulled cellulose acetate fibers.²¹

4342. Among the additions to a coagulating bath for cellulose ester or ether films used by Barthélémy are cyclohexanol, decalin, tetralin.²²

4343. Oxidation products of hydrogenated crude cresols, which comprise a mixture of α , β and γ -methyladipic acids together with lower homologs such as glutaric acid, are esterified as a whole with aliphatic, aromatic or cyclic alcohols to obtain products which may be used as substitutes for camphor in the manufacture of celluloid.²³

4344. Metallic resinates or linolates are dissolved in hydrogenized phenols, such as the cyclohexanols or their esters, or in cyclohexanone and its homologs, with or without the aid of other solvents. Solutions of resinates of aluminum, tin, zinc, manganese, and cobalt in cyclohexanyl formate constitute excellent siccatives. The solutions, with or without linseed oil or linseed oil varnish, can be used as vehicles in paints.²⁴

¹⁴ *Chem. Abst.*, 1923, **17**, 2791.

¹⁵ *Seifen. Ztg.*, 1928, **55**, 108.

¹⁶ *Ibid.*, 133.

¹⁷ *Brit. Pat.* 285,174, Nov. 19, 1926.

¹⁸ *Chem. Ztg.*, 1923, **47**, 727; *Chem. Abst.*, 1924, **18**, 1060.

¹⁹ *Rubber Age*, 1922, **12**, 205; *Chem. Abst.*, 1923, **17**, 900.

²⁰ *Brit. Pat.* 248,859, Dec. 16, 1924.

²¹ *Can. Pat.* 276,514, Dec. 20, 1927, to Brigg, et al.; *Chem. Abst.*, 1928, **22**, 2068.

²² *Brit. Pat.* 282,790, Dec. 28, 1927.

²³ *Chem. Abst.*, 1927, **21**, 1355; *Brit. Pat.* 250,910, Apr. 14, 1925, to Claassen; *Can. Pat.* 267,996, Feb. 1, 1927, to Claassen; *Chem. Abst.*, 1926, 1660.

²⁴ Friesenhahn, *Ger. Pat.* 334,761, July 25, 1919; *J.S.C.I.*, **1921**, 399A.

4345. Dreher proposes hexalin or tetralin in a binding agent for paints.²⁵

4346. Hydrogenated Phenol as Anti-knock. Cyclohexanol or other hydrogenated phenol is added to water-free motor fuels in the proportion of 5 per cent to reduce knock.²⁶

²⁵ French Pat. 636,827, June 29, 1927.

²⁶ Brit. Pat. 246,094, Jan. 19, 1925; *Chem. Abst.*, 1927, **21**, 488.

CHAPTER XLIV

HYDROGENATION OF COAL AND RELATED HYDROCARBONS

I

INTRODUCTORY AND EXPERIMENTAL

4400. Of recent years much time, money and energy have been spent on the problem of obtaining liquid fuel from coal. The total of the known and of the probable future potential supplies of petroleum is smaller than the quantity of coal known to exist in seams already explored. Nevertheless the former figure is stupendous, and the urge to convert coal into oil is due not to fear of imminent exhaustion of natural fuel oil sources but to the geographical distribution of the latter. Almost all naval steamships and a steadily increasing number of merchant vessels use liquid fuel for steam raising. Internal combustion engines of the Diesel type are being installed in a large percentage of new ships. Nevertheless, some of the greatest maritime countries must import all the fuel oil needed for their fleets. Some of these nations, e.g., Great Britain, France and Germany, have, however, rich domestic coal supplies. It is this combination of circumstances that has stimulated the search for a means of obtaining fuel oil from coal.

4401. A full account of the work done in this field in Germany up to 1925 will be found in Fischer's *Die Umwandlung der Kohle in Öle*.¹ More recent information, albeit somewhat vague and general, is contained in the Proceedings of two International Conferences on Bituminous Coal (1926 and 1928).

4402. The proportion of hydrogen in coal is always much lower than in the liquid hydrocarbons and other liquid fuels. It follows that the production of the latter from coal involves hydrogenation. This may take place by transfer within the molecules of the coal constituents, without hydrogen of *extrinsic* origin. The *intrinsic* hydrogenation is, evidently, limited and results in the production of volatile (gaseous and liquid) hydrogen-containing products and of a residue, poor in hydrogen, such as heavy tars and coke. This type of process, modified in various ways according to the end in view (production of illuminating gas, etc.), will not be dealt with here. We shall confine ourselves to the hydrogenation of coal with hydrogen of *extrinsic* origin. The indirect hydrogenation of coal, i.e., the production of water-gas and the conversion of the latter into methanol, hydrocarbons, etc., is the subject matter of a special section, viz., Chapters LII to LV.

¹ English translation with additions. *The Conversion of Coal into Oils*: New York, 1925. Van Nostrand Company.

EXPERIMENTAL

4403. The first attempt to hydrogenate coal was made by Berthelot,² some sixty years ago. His procedure was to treat finely powdered coal with saturated hydriodic acid solution at 270° C. for many (e.g., twenty-four) hours. The products were (calculated on the weight of coal): bituminous residue, 33 per cent; liquid hydrocarbons (mostly saturated, but including some cyclic compounds), 60 per cent. The gases consisted chiefly of hydrogen. The quantity of iodine released was twelve times the weight of the coal.

4404. Berthelot obtained similar results with wood and with lightly carbonized charcoal. With pure carbon, with coke and with fully carbonized charcoal the attempt failed.

4405. Many years later the method of Berthelot, modified by the addition of red phosphorus to the reacting substances, was used by Tropsch.³ This worker tested coals of various ages and found that, generally, the younger the coal the greater the susceptibility to hydrogenation. The result has since been confirmed by workers using other methods of hydrogenation. Anthracite (coke yield 89 per cent) treated by Tropsch's method during twelve hours at 200° C. yielded only 12 per cent of hydrogenated substances soluble in chloroform. At the other end of the series, a gas-flame coal (coke yield 64 per cent) gave 70.3 per cent of extract.

4406. Proceeding in the same way, but increasing the temperature and, therefore, the pressure, liquid hydrocarbons resembling petroleum were obtained. Gas-flame coal was extracted with chloroform and 0.5 g. of the residue was placed in a pressure tube with 1 g. of red phosphorus and 10 cc. of hydriodic acid (sp. gr. 1.7). The mixture was heated for six hours at 280° C. Petroleum-like liquids to the amount of 30 per cent of the weight of the coal resulted. The non-volatile bituminous residue was, for the most part, soluble in chloroform.⁴

4407. Hydrogenation with Sodium Formate. In a research carried out by Fischer and Schröder⁵ the source of hydrogen was sodium formate, which, on heating, readily liberates hydrogen and carbon monoxide. In blank experiments a given specimen of brown coal, heated under pressure at 400° C. for three hours, without addition of formate, gave the following results: without addition of water, ether soluble product, 1.3 per cent of the ash-free, dry coal: with addition of water, 10.1 per cent.

4408. The same coal under similar conditions, but with addition of twice its weight of sodium formate gave: without added water, ether soluble, 44 per cent of the ash-free, dry coal: with addition of water, 44.9 per cent.

4409. Further experiments showed that, in hydrogenation with formate, added water did not increase the yield. The optimum temperature was found to be 400° C. The ether extract, at this temperature, was a reddish-brown paste.

² *Bull. Soc. Chem.*, 1869, [2], 11, 278; *Ann. Chim.*, 1870 [4], 20, 526.

³ Fischer and Tropsch, *Abh. Kohl.*, 1917, 2, 154.

⁴ Fischer, *The Conversion of Coal into Oils*, New York, 1925, Van Nostrand Company, 177-179.

⁵ Fischer, *loc. cit.*, 179-187; Fischer and Schröder, *Brennstoff-Chem.*, 1921, 2, 161, 257; *Abh. Kohle*, 1920, 5, 470, 563.

The ether solution of this extract showed, always, a fine yellow-green fluorescence.

4410. This formate method was tried out on a large number of substances ranging from anthracite to cane sugar. The conditions of the experiment were the same in all cases. Four grams of the material were heated together with 8 g. of sodium formate and 8 cc. of water, to 400° C. for three hours, in a steel autoclave of 31 cc. capacity. The results are shown in the following table:

MATERIALS ARRANGED ACCORDING TO YIELD OF ETHER-SOLUBLE PRODUCTS OF HYDROGENATION ⁶

(In Per Cent of Organic Substance Used)

Bituminous Coal	Brown Coal	Peat, Wood, etc.
Anthracite..... 1.6		Charcoal..... 5.9
Fat coal..... 9.2		
Semi-coke..... 9.8		
Lean coal..... 10.7		
		Cellulose..... 12.9
		Cane sugar..... 17.3
		Fir wood..... 19.5
		Beech wood..... 19.6
		Lignin..... 22.3
		Peat..... 24.2
Fat coal (liable to spontaneous ignition) ... 26.3	Lignite..... 26.8	
Cannel coal..... 28.2	Semi-coke..... 32.4	
	Rosenthal coal..... 36.3	
	Ulmic acids..... 37.1	
Gas-flame coal..... 39.2	Saxon carbonizing coal.. 43.4	
	Rhenish brown coal... 45.0	

⁶ Fischer, *loc. cit.*, 184.

4411. The ether-soluble hydrogenated product from coal seems chiefly derived from the lignin constituent and is, therefore, composed mainly of cyclic hydrocarbons. On ultimate analysis the carbon content runs about 85 per cent, the hydrogen about 8 per cent. Fractionation of the product from a brown coal gave the results shown in the table below.

DISTILLATION OF ETHER-SOLUBLE PORTION OF HYDROGENATED BROWN COAL ⁷

Temperature, Degrees	Grams	Per Cent	Property of Distillate
100-200	0.28	4.1	Mobile.
200-250	0.64	9.4	Limpid.
250-300	0.71	10.4	Thicker.
300-350	3.31	48.6	Thin paste.
Residue	1.87	27.5	Solid, dark, opaque.
	6.81	100.0	

⁷ Fischer, *loc. cit.*, 186.

4412. Subjected to destructive distillation, without ether extraction, hydrogenated brown coal gave the following results:

DESTRUCTIVE DISTILLATION OF HYDROGENATED BROWN COAL ⁸

Experiment Number	Kind of Distillation	Product of Distillation	
		Tar Percentage of Ash-Free Dry Coal	Coke Percentage of Dry Coal
1	Ordinary	27.3	
2	Ordinary	26.6	
3	Ordinary	23.2	48.8
4	Ordinary	23.0	50.3
5	Ordinary	26.6	
6	Steam	35.1	53.1
7	21.9	61.1
8	Steam	30.0	51.3

⁸ Fischer, *loc. cit.*, 187.

4413. Hydrogenation with Hydrogen and with Carbon Monoxide. In the work epitomized in paragraphs 4407-4412 Fischer and Schröder depended on the thermic decomposition of formate to furnish the hydrogenating agents, hydrogen and carbon monoxide. They next carried out a research in which hydrogen and carbon monoxide were supplied, in gas form, from outside sources.

4414. In one series of six experiments, on Rhenish brown coal, in each case 20 g. of coal were heated for three hours to 400° C. in an iron autoclave. In the first experiment, the coal was heated alone; in the second, with water; in the third, with hydrogen; in the fourth, with hydrogen and water; in the fifth with carbon monoxide; in the sixth, with carbon monoxide and water. The gas pressures measured at room temperature were: hydrogen 130 atmospheres; carbon monoxide 140 atmospheres. The yield of ether-soluble hydrogenated product in the sixth experiment was about 30 per cent of the weight of the dry, ash-free coal. This was nearly 20 times the yield in the fourth experiment, which was the next best. Fischer attributes this superiority of carbon monoxide and water over hydrogen and water to the production of hydrogen in the nascent state by the interaction of carbon monoxide and steam. This is suggested by the fact that the sixth experiment gave the largest yield of carbon dioxide.

4415. At the end of this sixth experiment, the water was found overlying a yellow-brown layer of the consistency of petroleum jelly. There was also some black coal powder. These products were examined. The ether-soluble portion was fractionally distilled with superheated steam. There were thus obtained: brown, mobile oil, 15 per cent; yellow substance of buttery consistency, 40 per cent; soft, brown pitch, 12 per cent; residue in retort, 32 per cent. The black ether-insoluble powder gave up 53 per cent to boiling pyridine. One-quarter of the residue dissolved in boiling dilute hydrochloric acid, with evolution of sulphuretted hydrogen.

4416. This method was used, also, in comparative experiments with gas-flame coal, with semi-coke from bituminous coal, and with semi-coke from brown coal. In these experiments the gas pressure at room temperature was 90 atmospheres. Again, in each case, carbon monoxide was more efficacious than hydrogen. The semi-coke from bituminous coal proved refractory: even with carbon monoxide the ether-soluble product was only 0.58 per cent of the ash-free, dry coal. Very different was the behavior of semi-coke from brown coal, which yielded, with carbon monoxide, 22.37 per cent and, with hydrogen, 1.48 per cent of ether-soluble. Gas-flame coal gave 13.20 per cent with carbon monoxide and 10.47 per cent with hydrogen.

4417. Hydrogenation of Coke, Peat or Petroleum.⁹ The materials are hydrogenated by heating to 100° C. or more, under increased pressure, with carbon monoxide and water, or aqueous solutions, or suspensions.

4418. Influence of Pressure. In experiments of this kind, using Rhenish brown coal, increasing the gas pressure, in the case of hydrogen from 50 atmospheres to 90 atmospheres and, in the case of carbon monoxide, from 50 atmospheres to 140 atmospheres, was found to have only a moderate effect on the yield of ether-soluble product. Thus, with carbon monoxide, at 50 atmospheres the yield was 22 per cent; at 90 atmospheres it was 25 per cent; at 140 atmospheres it was 29.7 per cent. With hydrogen, at 50 atmospheres it was 17.4 per cent; at 90 atmospheres it was 21.8 per cent.

4419. Influence of Temperature. Experiments made with a view to ascertaining the optimum temperature, while not entirely consistent in their results, point to a temperature between 350° C. and 450° C. as the best. With carbon monoxide at 140 atmospheres the yields of ether-soluble products were: at 300° C., 8.8 per cent; at 350° C., 19.6 per cent; at 375° C., 25.9 per cent; at 400° C., 29.7 per cent.

4420. Autoclave Material. Iron is known to be an active catalyst of the conversion of carbon monoxide to the dioxide in the water-gas reaction. If it is true that the superior efficacy of carbon monoxide is due to the production of nascent hydrogen in the body of the coal-water-gas mixture, that part of this valuable reaction which would take place at the wall of an iron autoclave would thereby be lost. Comparative tests with iron and with copper autoclaves failed to furnish evidence of this effect. At 350° C. the copper and, 400° C., the iron vessel gave the better yield.

4421. Influence of Water. Twenty grams of brown coal were heated with carbon monoxide under 140 atmospheres original pressure, for three hours at 400° C., with varying quantities of water. With 10 cc. of water the yield of ether-soluble products was 2.20 g. (13.9 per cent); with 20 cc. of water, 4.65 g. (29.4 per cent); with 40 cc. of water, 5.56 g. (35.1 per cent).

4422. Summary. In the hydrogenation of coal with carbon monoxide and water the completion of the process is favored by increase in the gas pressure, in the quantity of water, and, up to a certain point, in the temperature. In the

⁹ Ger. Pat. 382,367, Oct. 24, 1920, addition to 370,975 to Fischer and Schröder.

conditions of these experiments carbon monoxide is more efficacious than molecular hydrogen, though less so than sodium formate.

4423. Hydrogenation of Lignite by Means of Carbon Monoxide in Presence of Ammonia and Pyridine. The hydrogenation of lignite (union briquettes) by means of carbon monoxide and water in presence of ammonia or pyridine, added to increase the stability of the formic acid produced as intermediate product, gave no greater yield of hydrogenation product soluble in ether than former experiments without the addition of these bases.¹⁰

4424. Powdered coal and finely divided iron are injected into a reaction chamber together with steam. Hydrogen is obtained from the steam and iron, and reacts with the coal at 25–30 atmospheres and 400° C. Any carbon dioxide formed may be absorbed by lime, and hydrocarbons are obtained. The reaction chamber may be of catalytic material such as nickel.¹¹

4425. Hydrogenation with Sodium Carbonate and Hydrogen. Schröder having observed that formate is produced by heating sodium carbonate solutions with hydrogen under pressure,¹² Jaeger, at Fischer's suggestion,¹³ investigated the possibility of using this reaction to replace preformed formate, or carbon monoxide and hydrogen in the hydrogenation of coal.

4426. Twenty-five grams of Rhenish brown coal were heated with 100 cc. of normal sodium bicarbonate solution for two hours to 400° C. at various hydrogen pressures. At 20 atmospheres the yield of ether-soluble product was 10 per cent; at 60 atmospheres it was 19 per cent; at 100 atmospheres 36 per cent. Further experimentation showed that both the bicarbonate and the water were essential. The most favorable temperature was again found to be 400° C.

4427. The coal residue was caked and therefore the contact with the reaction mixture was poor. Shaking at 300° for two hours with an initial hydrogen pressure of 30 atmospheres gave 8.4 per cent of ether-soluble; four hours at 60 atmospheres initial gave 12.6 per cent, ether soluble. Owing to the fact that the maximum pressure admissible with the shaking autoclave was 150 atmospheres, temperatures higher than 300° C. could not be used in presence of water.¹⁴

4428. Legé's¹⁵ process seems to be related to this line of work. Coal, alkali or alkaline-earth salts, alkali or alkaline-earth carbonates, and water are allowed to interact under pressure and at the necessary temperature. After being brought into contact with alkali or alkaline-earth chlorides in a further working chamber, the gas mixture produced is allowed to interact at 400°–700° C. in the presence of iron and other metals or metallic oxides as catalysts, then passed over iron or copper at 300°–400° C., and the products condensed in the solid or liquid form. The residual gases are used for heating purposes.¹⁶

4428A. Plauson^{16a} proposes heating a caustic soda emulsion of carbonaceous material under pressure with hydrogen or a gas such as carbon monoxide or nitrogen.

4428B. A process^{16b} for obtaining low-boiling products utilizable as benzine substitutes consists in mixing in approximately equal proportions brown coal and hydrocarbon such as

¹⁰ Schröder, *Ges. Abh. Kennt. Kohle*, 1921, 6, 188; *Chem. Zentr.*, 1924, 95, I, 839.

¹¹ *Chem. Age* (London), 1927, 16, Apr. 30; Brit. Pat. 266,311, to Gaertner (International Convention date February 18, 1926).

¹² Schröder, *Ges. Abh. Kennt. Kohle*, 1921, 6, 77.

¹³ Fischer, *loc. cit.*, 195.

¹⁴ Cf. Fischer and Jäger. Hydrogenation of lignite with hydrogen in presence of sodium bicarbonate, *Ges. Abh. Kennt. Kohle*, 1925, 7, 141; *Chem. Abst.*, 1927, 21, 4047; Fischer and Pichler. Formation of gaseous and liquid hydrocarbons by the action of steam and alkali on semi-coke, *Brennstoff-Chem.*, 1928, 9, 200; *Chem. Abst.*, 1929, 23, 1384.

¹⁵ French Pat. 602,007, Nov. 17, 1924.

¹⁶ *Brit. Chem. Abst.*, 1927, 516B.

^{16a} Vielle and Plauson, Brit. appln., 160,789, not accepted, date March 21, 1921.

crude naphtha. The mixture is finely ground and from 3 to 5 per cent of alkaline earth nitrate is added. It is then sprayed into a distillation chamber in the presence of an air-steam mixture heated to 600–700°, whereby it is decomposed. The conversion amounts to only 4 per cent for the coal and 18 per cent for the naphtha.

4429. The Production of Ammonia and Hydrocarbons from Lignite Coke. Hoffmann and Groll¹⁷ discuss the action of steam at 500° C. on lignite coke, with description of experiments with various catalysts.

4429A. Fischer and Pilcher¹⁸ were unable to confirm the statement of Hoffmann and Groll that hydrocarbons could be made by passing nitrogen with steam over activated lignite coke mixed with various metal and oxide catalysts.

BERGINIZATION¹⁹

4430. The hydrogenation of coal at high temperatures with hydrogen at high pressures is usually associated with the name of Bergius, and the convenient term "berginization" is now frequently applied to this kind of process.

4431. Before, however, describing Bergius' own processes we must deal with some experiments which were made after he had applied for his earliest patent, but before the contents of his specification were made public. In 1914 Fischer and Keller²⁰ experimented with the destructive distillation of bituminous coal under high hydrogen pressure. These experiments showed: "First, that the tar or oil yields, at high hydrogen pressure, are several times greater than those obtained at ordinary pressure; and secondly, that, even at 500° C., the amount of coke residue is inversely proportional to the hydrogen pressure, so that with rising hydrogen pressure the formation of volatile constituents, and mainly of methane, increases."²¹

4432. While investigating the thermal decomposition of heavy hydrocarbon oils at high pressures, Bergius observed that by subjecting such oils to a temperature of 450° C., under a hydrogen pressure of over 20 atmospheres, he was able to produce petroleum spirit consisting of saturated hydrocarbons.²² Later he specified an initial hydrogen pressure of 100 atmospheres, measured at room temperature. This at 450° C. would give pressures much over 200 atmospheres.²³

4433. Bergius had already made an artificial coal²⁴ by heating cellulose for eight hours at 340° C. under a pressure of 100 atmospheres.²⁵ He now applied to this product the method of hydrogenation which he had successfully used with heavy hydrocarbon oils. By heating this artificial coal at 400° C. in a bomb with hydrogen, he obtained a 70 per cent conversion to a product soluble in benzene. On evaporation of the solvent the residue was similar to a natural mineral

¹⁶ Brit. Pat. 4340, July 29, 1915, to Plauson and Schröder.

¹⁷ *Z. angew. Chem.*, 1927, **40**, 282; *Chem. Abst.*, 1927, **21**, 1880.

¹⁸ *Brennstoff-Chem.*, 1927, **8**, 307.

¹⁹ Where processes are applied both to coal (or coal products) and to petroleum, they will be dealt with partly in this section and partly in subsequent chapters.

²⁰ *Ges. Abh. Kennt. Kohle*, 1916, **1**, 148.

²¹ Fischer, *loc. cit.*, 197.

²² Ger. Pat. 304,348, 1913; U. S. Pat. 1,344,671, June 29, 1920.

²³ Brit. Pat. 4574, 1914.

²⁴ *J.S.C.I.*, 1913, 462B.

²⁵ Cf. Tropsch and Philippovitch. Artificial production of coal from cellulose and lignin in the presence of water. *Ges. Abh. Kennt. Kohle*, 1925, **7**, 84; *Brit. Chem. Abst.*, 1926, 858B.

oil. The application of this discovery to the hydrogenation of natural coal was a short and obvious step.

4434. Berginization of Coal. Probably the first patent disclosing the application of the Bergius process to coal is the British patent 18,232, of Aug. 1, 1914.²⁶ It is described as a "Process of treating coal and similar substances to obtain oils, ammonia and other products." The coal or other solid carbonaceous material is subjected to the action of hydrogen at pressures above 10 atmospheres, and to a temperature between 300° and 500° C. Under these conditions the hydrogen reacts directly with the coal, and forms without production of uncondensable gases, valuable hydrocarbons, which are either liquid at ordinary temperatures and pressures, or have low melting-points. In place of hydrogen, gases containing hydrogen, such as water-gas, may be employed, or substances which yield hydrogen, such as calcium hydride, may be used. It is advisable to operate the process in the presence of a solvent for the products formed during the reaction, petroleum distillates being suitable for this purpose. The nitrogen of the coal is recovered in the form of ammonia in the reaction vessel.²⁷

4435. The following details are taken from the description given by Bergius and Billwiller. On heating coal with hydrogen to a temperature between 300° and 500° C., at pressures up to 200 atmospheres, the hydrogen combines with the coal, forming hydrocarbons which are liquid at ordinary temperature or have a low melting-point. Only a very small amount of methane is produced. Thus, they obtain distillates from coal amounting to nearly 100 per cent of the carbonaceous substance, whereas by the usual method of distilling coal the liquid products usually do not exceed 3 per cent. The nitrogen contained in the coal is transformed into ammonia. Some bodies of the phenolic type are produced. The reaction is shortened if a solvent such as benzine is employed. The process is applicable to the treatment of wood, peat, tar and pitch in like manner. Bergius and Billwiller give several illustrations of the method of procedure, the following being noted: 1. Four hundred kilograms powdered coal are filled into a pressure-resisting vessel of about 400 liters capacity, which is connected to a tank in which hydrogen is held under 200 atmospheres pressure. After fifteen hours the connection with the hydrogen tank is turned off and the vessel is emptied. About 10 to 15 kg. of hydrogen have been then consumed, according to the quality of coal used. From the contents of the vessel more than half of the coal can be separated from solid residue as liquid. The remaining part of liquid products in the solid residue can be gained by extraction. 2. One hundred and fifty kilograms powdered coal are placed with an equal quantity of heavy benzine in a pressure-resisting vessel of about 400 liters capacity, connected to a hydrogen tank. For the purpose of mixing, the vessel is rotated. After twelve hours, at a temperature of 400°, the vessel is opened and the liquid produced is separated from the solid residue. Only 15 per cent of the weight of

²⁶ The application date of the corresponding German patent is Aug. 8, 1914.

²⁷ *J.S.C.I.*, 1916, **35**, 167. See also *J.C.S.I.*, **1920**, 743A; U. S. Pat. 1,342,790, June 8, 1920 (assigned to Chem. Found., Inc.); U. S. Pat. 1,251,954, 1918, to Bergius and Billwiller; Brit. Pat. 148,436, 1920.

coal employed is then left. The remaining 85 per cent is dissolved in the solvent. The consumption of hydrogen is about 5 kg.

4436. It will be noticed that already at this early date Bergius was mixing the coal dust with a "solvent." Later this oily admixture acquired a new and important function. It appears that in 1913 Bergius was working a batch and not a continuous process. When he developed a continuous process the added oil served to render the mass pumpable. Nevertheless its earlier function as a solvent of the reaction products was and remained essential to the completion of the hydrogenation. Powdered coal (clarain) alone heated to 400° C. for twenty-nine hours, under a maximum hydrogen pressure of 154 atmospheres in a rotating autoclave absorbed only a small amount of hydrogen; it remained solid but was found to yield 11 per cent of matter soluble in chloroform.²⁸

4437. Durcy has a process for the production of hydrocarbons resembling natural petroleum in which bituminous coal, lignite, tar, heavy oils, or vegetable or animal oils are hydrogenated by heating with hydrogen or other hydrogenating gas to pressures between 200 and 800 kg.²⁹

4438. Nash and Shatwell³⁰ found that coal could not be berginized when heated alone with hydrogen, but liquefaction was obtained when a "solvent" such as phenol or heavy mineral oil was used. Owing to the difficulty of separation when oil was used (in an experiment with clarain) phenol was substituted. Clarain with phenol, three hours at 416° C., 123 atmospheres hydrogen pressure, absorbed 2 per cent hydrogen, gave 56.2 per cent phenol soluble, 20 per cent insoluble, 23.8 per cent loss. Treated for thirteen hours at 416° C., 150-160 atmospheres, a like mixture absorbed 5.48 per cent hydrogen. Thirty-seven per cent of the coal had been liquefied. Substituting nitrogen for hydrogen produced only 8.3 per cent phenol soluble. Durain with phenol treated for ninety-six hours, with daily renewal of the hydrogen, absorbed 3.8 per cent hydrogen, giving 45 per cent insoluble residue. Fusain (95 per cent carbon, 2 per cent hydrogen) showed almost no berginization.³¹

4439. Working on the same lines Skinner and Graham³² report that a German brown coal, two Devonshire lignites, and semi-coke prepared from the last two at 440°, mixed with twice their weight of phenol, were hydrogenated at about 415° under about 120 atmospheres pressure for about eight to twelve hours. The resulting products were extracted from the autoclave and all the phenol-soluble products removed. These were precipitated by caustic soda and there were separated an oil and a flocculent precipitate, which were extracted with chloroform, in which the solid was insoluble. In this manner yields and analyses of the phenol-insoluble residue, phenol-soluble, chloroform-soluble brown oil, and

²⁸ Shatwell and Graham, *Fuel*, 1925, 25-30. See Waterman and Doting, *Chimie et industrie*, 1929, Spec. No., 218; *Chem. Abst.*, 1929, **23**, 3559.

²⁹ *Brit. Chem. Abst.*, **1927**, 273B; French Pat. 607,688, Mar. 23, 1925.

³⁰ *Colliery Guardian*, 1924, **128**, 1435; *Chem. Abst.*, 1925, **19**, 1188.

³¹ The same and similar work is reported by Shatwell and Graham in *Fuel in Science and Practice*, 1925, **4**, 25, 75, 127; more analytical data are given. Bergius' claims are confirmed, but not his statement that 85 per cent carbon content is the limit for berginization. The heavy losses on clarain and durain are attributed to gas, water and phenols.

³² *Fuel*, 1925, **4**, 474.

phenol-soluble, chloroform-insoluble brown powder were obtained. Ash content does not seem to affect the result much; Fischer's observation that the oil yield is increased by the presence of water is substantiated; hydrogenation appears to take place by the addition of hydrogen to molecular groupings in both the original substances and their cokes, and by the addition of hydrogen to the products of thermal decomposition at the moment of formation. Bergius' claim that complete conversion of a coal can be obtained if its carbon content is less than 85 per cent is not confirmed, although the conditions of hydrogenation were admittedly less drastic than those used by Bergius.³³

4440. Bohemian waxcoal (corona) 600 grams, was subjected to berginization in a 5-liter revolving autoclave at 200 atmospheres and 400°–450° C. Apparently no "solvent" was used. After two hours' treatment a 50 per cent yield of liquid was obtained.³⁴

4441. Work done at the Mines Research Laboratory, Birmingham (England) and reported by Graham,³⁵ failed to confirm the view of Bergius that the quality of the coal was of minor importance. The best results were obtained with para-bituminous coals (Seyler's classification). But on the whole the results were less favorable than those reported by Bergius. On this point the work was criticized by Ormandy, firstly, because of the non-continuous nature of the Birmingham experimental plant and, secondly, because of the use of phenol as a solvent.³⁶

4442. In two reports Graham and Skinner³⁷ describe this work on berginization in detail. Coal samples (60-mesh) were treated in a 3-liter steel autoclave, gas-heated and rotated at about 60 r.p.m. In all experiments 200 g. of coal were used suspended in 100 g. of phenol. The maximum pressure during hydrogenation was 145–150 atmospheres, the temperature was kept at about 430°, and the total duration of heating was eight hours carried over two days, the hydrogen being renewed. The products of reaction were first distilled in an aluminum retort up to 150°. The light spirit fraction was washed with dilute caustic solution and the remaining products were further treated with chloroform, thus yielding (a) phenol-insoluble, (b) phenol-soluble, chloroform-insoluble, and (c) phenol-soluble, chloroform-soluble fractions. Products (c) were further separated into fractions distilling up to 300°, and between 300° and 450°. The results show yields varying from 5.8 to 109 gal. of total oil per ton of coal, corresponding to gasoline yields of 2.8 to 23.9 gal. per ton of original coal. The addition of ferric oxide as catalyst to the original charge increased the gasoline yield from an equivalent of 9.5 to 15 gal. per ton of coal; there was also an increase in tar oil and amount of aqueous liquor produced, but the yield of product (b) was practically unaffected. In general, the yields of tar oil (product c) are less than those obtained by Bergius. The effect of raising the hydrogen pressure was to increase the yield of tar oil. The solid residue left after hydrogenation averages about 20 per cent, and the yield of gaseous products is about 20 per cent by weight of the original coal. The general conclusions are that gasoline suitable for internal-combustion engines may be obtained, on an average, in amount up to 25 gal. per ton of coal treated. The value of the heavier oil, however, is not so assured. Certain coals have proved to be more suitable for treatment than others, and these appear to fall into the para-bituminous division of the Seyler classification. Those having a carbon : hydrogen ratio between 15.5 and 16.5 appear to give the highest oil yields. From calculations of the costs of the process it is considered that such coals could possibly be worked at the present time with profit.³⁸

³³ *Brit. Chem. Abst.*, 1925, 947B.

³⁴ Novák and Hubáček, *Paliva a Topeni*, 1927, 9, 145; *Chem. Abst.*, 1928, 22, 4228. The effects of various catalysts are reported, as also is the chemical character of the products.

³⁵ *Chem. Age* (London), 1929, 20, 25.

³⁶ Cf. Lush's remarks which were prompted by this discussion, para. 4445.

³⁷ *J. Inst. Petrol. Tech.*, 1928, 14, 78; *Fuel*, 1928, 7, 543.

³⁸ *Brit. Chem. Abst.*, 1928, 557B. Note that the gallon here mentioned is the imperial gallon of 160 ounces—not the U. S. gallon of 128 fluid ounces.

4443. The addition of ferric and nickel oxides increased the oil yields appreciably, but the most effective catalyst for this purpose was ammonium molybdate. The results of the hydrogenation of Warwick slate vitrain and of the residue after extracting the coal with phenol at 185° indicate that the extract is not converted into oil in the process, but appears in the phenol-insoluble residue. On the other hand the pyridine-soluble constituents of a Staffordshire coal appeared to be completely converted into oil. Fine grinding of the coal increases its tendency to coke during the process. The phenol-insoluble residue is richer in carbon, and generally, but not always, poorer in hydrogen than the original coal. On carbonizing this residue at 600° usually only a powdered coke was produced; the products from Warwick slate vitrain and from Graigola coal, however, produced coherent cokes, the latter giving a more strongly swollen coke than the original coal.³⁹

4444. Comparative experiments with boghead coal and with true cannel coal have led Skinner and Graham to the conclusion that neither the former, nor Scotch shale which resembles it, would repay efforts to berginize it.⁴⁰ All this work must, however, be taken with the reserves indicated by Ormandy (para. 4441). Even if they are conclusive in regard to Scotch shale this is not universally true of oil shales for Kogermann⁴¹ reports distinctly more encouraging results with Estonian oil shales. True, the total yield of oil was not increased on hydrogenation, but the quantity of light oils was greater and these were more saturated. The phenolic content was decreased.

4444A. An examination of the products of the hydrogenation of Siberian boghead coals, together with results of the action of alcoholic potassium hydroxide on these coals, leads to the conclusion that they consist of saturated and unsaturated monocarboxylic acids of the aliphatic series, of cyclic and polycyclic acids, and of neutral oxygenated compounds of cyclic structure. On hydrogenation the cyclic acids eliminate carbon dioxide and are transformed into cyclic hydrocarbons. The products of hydrogenation contain no phenols.^{41a}

4445. Lush⁴² has commented on the propriety of using phenol as a solvent or suspension medium in experimental berginization. Not only is phenol a product of the process but it is, under the conditions prevailing, readily converted to cyclohexane. Lush himself reports that he has converted several gallons of phenol to cyclohexane at 160° C. and under 15 atmospheres pressure, conditions far milder than those used in berginization. This involves absorption of hydrogen, and cyclohexane is a constituent of "Bergin spirit." Now Ormandy has reported the formation of 20 per cent of phenols in berginization, while Graham, using phenol as solvent, found an increase of only 4 per cent. Lush's remark on this is that we may here have the mass action of the solvent phenol depressing the normal formation of phenols. This has two bearings, one theoretical, the other practical. First, it may be seen as supporting, by analogy, the view that the essential rôle of the hydrogen itself is to suppress the formation of the 3-4 per cent of hydrogen normally present in gas from high-temperature carbonization. Second, it may afford a method of controlling the nature of the product, by putting undesired substances into the reaction mixture in equilibrium proportions.

³⁹ *Brit. Chem. Abst.*, 1929, 81B.

⁴⁰ *Fuel*, 1927, 74; *Brennstoff-Chem.*, 1927, 175.

⁴¹ *Petr. Times*, 1927, 18, 903; *Chem. Abst.*, 1928, 22, 680.

^{41a} Stadnikov and Kashtanov, *Brennstoff-Chem.*, 1929, 10, 417-419; *Brit. Chem. Abst.*, 1930, 57A.

⁴² *J.S.C.I.*, 1929, 48, 112.

4446. To this matter of phenol formation and hydrogenation during berginization the observations of Fischer and Tropsch ⁴³ on the behavior of cresols are directly relevant.

The reduction of *o*-, *m*-, and *p*-cresol by hydrogen under pressure proceeds very slowly, with the formation of phenol, toluene, and methane and its homologs, showing that a reduction to hydrocarbons as well as the splitting off of the methyl group has taken place. The speed of the reaction is so slow, however, that it is impossible for the phenols formed in the primary decomposition of coal to be appreciably acted upon by hydrogen during the Bergius process.⁴⁴

4446A. Dunstan,⁴⁵ however, reports that cresylic acid can be reduced substantially to hydrocarbon by simple cracking in the vapor phase at 750° C., without hydrogen and without pressure. The difference between this result and those of Fischer and Tropsch is, perhaps, a matter of temperature.

4447. Kling and Florentin ⁴⁶ offer as an explanation of berginization, that for every complex organic molecule there is a temperature at which it begins to split into simpler molecules and that, in many cases, this corresponds to the temperature at which, under the hydrogen pressures used, these simpler molecules can be hydrogenated. They propose to found, on this hypothesis, a general method for the investigation of the structure of complex molecules.

4448. In this connection should be read a paper by Spilker and Zerbe.⁴⁷ These workers treated naphthalene, anthracene, phenanthrene, acenaphthene and fluorene with hydrogen at various temperatures and pressures. Their results tend to support the views of a number of observers. There was a limiting temperature for each substance, at a given pressure, at which molecular disintegration occurred. The berginization at this point went in two ways. On the one hand the disintegrating, unstabilized molecule was hydrogenated, with the production of hydroaromatic compounds. On the other, the fragments were also hydrogenated, yielding gaseous and liquid products. These or analogous changes occurring in an atmosphere of hydrogen, known variously by the terms *hydrofission*, *hydroscission* and *hydrocleavage*, will be considered further in subsequent chapters.

4449. Kling and Florentin reiterated and expanded their views in 1928 at the Second Pittsburgh Conference on Bituminous Coal. They said that in berginization of coal two components underwent hydrogenation in different manners. The first rather readily yielded aliphatic compounds; the second, derived from lignin, was resistant to berginization and only with aid of catalysts could it be hydrogenated. Phenols, according to Kling and Florentin, were almost completely refractory to simple berginization, i.e., to treatment with hydrogen at high temperatures and pressures, but without catalysts.

4449A. According to Ipatiev,^{47a} tests of pyrogenic decomposition made with hydrogen under pressure gave substances more hydrogenated than the starting materials and brought out the catalytic effect of the metal of which the autoclave was constructed. Orloff and Petroff found from similar investigations that complete hydrogenation of a molecule at 450°

⁴³ *Brennstoff-Chem.*, 1926, **7**, 2.

⁴⁴ *Brit. Chem. Abst.*, 1926, 148B.

⁴⁵ Second Internat. Conf. Bitum. Coal, 1928.

⁴⁶ *Compt. rend.*, 1926, **182**, 389; *Chem. Abst.*, 1926, **20**, 1587.

⁴⁷ *Z. angew. Chem.*, 1926, **39**, 1138; *Chem. Abst.*, 1927, **21**, 166.

^{47a} *Chaleur et industrie*, Aug., 1929, p. 377; *Univ. Oil. Prod. Co. Bulletin*.

and 80-100 atmospheres pressure at the start can only be accomplished in exceptional cases. A partial hydrogenation, with preservation of the carbon skeleton, is only possible for combinations of aromatic chains, as in naphthalene, phenanthrene, anthracene, etc. Upon hydrogenation, the chains are broken, the groups at the moment of forming unite with hydrogen, and if contact is long enough decomposition will proceed farther. For the hydrocarbons mentioned above the final products will be methane and benzol. The simpler hydrocarbons, containing no condensed nuclei, behave as in ordinary cracking except that the production of unsaturated hydrocarbons will be small. The products will therefore be of low molecular weight because the conditions requisite for polymerization do not exist. Substances containing oxygen, such as phenols and ketones, are reduced to the corresponding hydrocarbons. The compounds of nitrogen lose this element in the form of ammonia, the sulphur compounds their sulphur in the form of hydrogen sulphide. The latter can be retained by adding metallic oxides to the mass being treated. The catalyst lowers the temperature of partial hydrogenation or of dissociation so that hydrogenating reactions take place at temperatures below limits at which the hydrocarbons could no longer exist. Without the catalyst and at a given temperature the hydrocarbons before combining with the hydrogen or being decomposed by it may undergo complete modification of their chemical structure. Byproducts of little value for making coke can thus be transformed into light benzolic hydrocarbons. Birchwood tar yields considerable amounts of motor fuel. Under the influence, then, of high temperature and of hydrogen under pressure, Ipatiev concludes that unsaturated hydrocarbons are saturated, their oxygen derivatives are reduced, complex molecules dissociate, and the products of dissociation unite with hydrogen to form light oils.

4450. Levi, Padovani and Amati ⁴⁸ had for primary object the exploration of the resources of Italy in petroleum, bituminous schists, asphaltic limestone and the like, susceptible of berginization. The points of general interest in their results are that in simple cracking the end pressure was always greater than the initial (atmospheric) pressure, while in berginization there was always a fall in pressure, notwithstanding the formation of non-condensable gases. Further, there was no notable difference in the degree of unsaturation of the gases in the two cases. But the quantity of saturated gases produced by simple cracking is much the greater. This recalls the views expressed by several investigators that anti-dissociating action of hydrogen under high pressure and at high temperatures is a more essential feature of berginization than is its saturating power.⁴⁹

4451. Varga ⁵⁰ hydrogenated an eocene brown coal under berginization conditions, except that he used no solvent.

The rate of heating was such as to reach the reaction temperature in seventy-two to seventy-seven minutes, and the bomb was then maintained at this temperature for one minute, one hour, or three hours. On account of the high sulphur content of the coal (3.98 per cent) it was necessary to add 15 per cent of iron oxide in order to obtain a gas free from hydrogen sulphide and an oil with a minimum sulphur content (0.22-0.29 per cent). This large addition of iron oxide had a catalytic effect on the process, lowering the temperature of hydrogenation and increasing the yield of oil. From 16.8 to 57.9 per cent of the coal was converted into oil, the best yields being obtained with only a short heating period (one minute) after reaching the reaction temperature. On further heating the oil was more or less (up to 50 per cent) decomposed again. The maximum conversion into oil (57.9 per cent) was obtained with a charge of 300 g. of coal at 470° and an initial pressure of 100 atmospheres. The yield fell off when the charge was increased.⁵¹

4451A. Von Makray ^{51a} reports that with 2200 g. of dry pulverized brown coal, together

⁴⁸ *Atti II Congr. naz. chim. pura appl.*, 1926, 530; *Chem. Abst.*, 1928, **22**, 2261.

⁴⁹ Cf. Levi, *et al.*, Study of [hydrogenation of] lignite of Ribolla. *Ann. chim. applicata.*, 1927, **17**, 491; *Chem. Abst.*, 1928, **22**, 677.

⁵⁰ *Brennstoff-Chem.*, 1928, **9**, 277.

⁵¹ *Brit. Chem. Abst.*, 1928, 774B; *Chem. Polyöirat*, 1928, **34**, 65-76; *Chem. Abst.*, 1929, 4796.

^{51a} *Brenn Chem.*, 1930, 61; *Univ. Oil Prod. Co. Bulletin*; *Brit. Chem. Abst.*, 1930, 354B.

with 330 g. of iron oxide and iron balls to give better mixing, and using hydrogen at 110 atmospheres pressure, and a temperature of 470° C., 45–46 per cent of the coal was converted into benzol-soluble substances. Of the total 2723.4 g. of materials used 2717.4 g. was recovered. Of the total carbon introduced into the reaction 53.4 per cent was found in the oil, 21.7 per cent in the gas, and 24.6 per cent in the insoluble residue. According to the gas analysis no carbon monoxide was formed in the reaction. The oil contained 29.8 per cent of the hydrogen introduced, 21.8 per cent remained unchanged in the gas, the rest was distributed between the water formed, the gaseous hydrocarbons and the insoluble residue. The hydrogen consumed in reducing the iron oxide and the organic oxygen compounds was only 2.9 per cent of the total hydrogen. The water formed came mainly from the organic oxygen compounds. Less water of decomposition was formed than in the low-temperature carbonization of the coal at 500° C. (932° F.). The iron oxide took up 96.7 per cent of the sulphur in the charge of coal. The oil contained only 0.39 per cent of sulphur. Of the nitrogen content of the coal 41.0 per cent was found in the form of ammonia and 31.4 per cent in the form of bases in the oil. Only a small quantity of the nitrogen introduced came out as gaseous nitrogen. Carbon dioxide formed accounted for 46 per cent of the oxygen, water for 35.6 per cent. The oil contained 15.5 per cent of the total oxygen in the form of phenols.

4452. Oshima and Tashiro ⁵² find that, in berginization of coal, the temperature and pressure curves have two points of change: at one the temperature tends to fall in spite of continued heating; at the other rising temperature causes no increase in pressure. They suggest that not only the temperature and pressure of maximum oil yield should be maintained, but the conditions which afford the largest yield of the valuable lighter oils.

4453. Pyhala ⁵³ has noticed that, in the distillation of petroleum residues at ordinary pressures, two decomposition points occur marked by rapid distillation. The two points are at 380°–410° C. and 430°–450° C. High percentages of paraffin and asphalt are stated to be decomposed without coke formation. The decomposition may be controlled by regulating the rate of temperature rise. Pyhala speculates as to the possible significance of these facts in connection with the mechanism of berginization.

4454. Berginization of Cottonseed Oil. Waterman and co-workers have contributed a valuable series of investigations bearing on berginization. Comparing the decomposition of cottonseed oil in a closed vessel at 450° C. (cracking) with the treatment of this oil with hydrogen under pressure at the same pressure (berginization) Waterman and Perquin ⁵⁴ point out that in the berginization of products containing carbon and hydrogen one has only to deal with two processes—the process of cracking and the process of hydrogenation. In this case, however, the matter was somewhat more complicated because here the hydrocarbons must first be formed from fats. The change of the pressure during berginization is essentially different from that in cracking. The rise of the pressure is considerably smaller in berginization than in cracking. It appears from the gas analysis that the oxygen of the cottonseed oil is driven out in both cases almost quantitatively as carbon monoxide, carbon dioxide and water.

4454A. Both by cracking and by berginization cottonseed oil can very efficiently be converted into hydrocarbon mixtures with high gasoline percentage.

⁵² *J. Fuel Soc., Japan*, 1928, **7**, 70.

⁵³ *Petrol. Z.*, 1928, **24**, 308; *Chem. Abst.*, 1928, **22**, 3765.

⁵⁴ *Verslag Akad. Wetenschappen Amsterdam*, 1923, **32**, 871; *Chem. Abst.*, 1924, **18**, 1397; *J. Inst. Petrol. Tech.*, 1924, **10**.

4454B. In these experiments, according to Waterman, the behavior of the cottonseed oil is not very different from that of a hydrocarbon mixture, as the oxygen can easily be eliminated from it. In the berginization of the cottonseed oil very much hydrogen is consumed; among other ways directly or indirectly in the formation of water. However, the conclusions based on the results obtained with cottonseed oil scarcely permit of direct application to hydrocarbons. Ordinary pyrolytic cracking of petroleum hydrocarbons with its concomitant of deep-seated polymerization involves a very different series of reactions from those of *hydrogenolysis* concurrent alteration by *hydrocleavage* or *hydroscission*.

4454C. In both processes Waterman reports that the formation of coke takes place (about 7 per cent in cracking), this being considerably less in berginization (0.3–0.5 per cent). The high-pressure hydrogenation of petroleum is in a considerable measure one of *hydrocarbonization*, that is, various compounds containing nitrogen, oxygen, sulphur, and the like, present in the petroleum are reacted upon by hydrogen and *hydrocarbons* formed therefrom. Coking to the degree noted by Waterman ordinarily does not take place. In fact, as will be more fully considered in a subsequent chapter relating to the hydrogenation of petroleum, hydrogen under the conditions of commercial performance appears to have a selective action on asphalts and tars, converting black oils to colorless products. (See also work of Waterman and associates on paraffin wax, paras. 4456–4460.)

4455. Light Hydrocarbons from Animal and Vegetable Oils. Kling and Florentin have described the application to animal and vegetable oils of a process analogous to berginization for the production of light saturated hydrocarbons. The material is treated with hydrogen under 45 kg. per square centimeter pressure (about 42 atmospheres) at 350°–480° C., in presence of a dehydrating catalyst such as thoria, alumina, and silica.⁵⁵

4456. Berginization of Paraffin-wax. Much of the work of Waterman and his associates was done on paraffin wax. Paraffin wax is much more easily evaluated than asphalt, and this holds also for the products prepared from paraffin when they are compared with the corresponding substances formed in the treatment of asphalt. Thus paraffin yields products that are less strongly colored than Mexican asphalt. The paraffin wax had a specific gravity at 15°/15° C. of 0.913, the solidifying point (Shukoff method) was 50.6° C.; the bromine value (addition) was 0.5 and could therefore be neglected. The temperature of the experiment was 435° C. The work was done in a continuously shaken autoclave. Stones were put in the autoclave to promote mixing. The oils obtained by the Bergius process were colored from yellow to red and perfectly transparent; a small quantity of "carbon" was deposited on the bottom. The oils obtained in cracking were very dark of color and opaque. Here, too, separation of some carbon was found.

The quantity of carbon which is deposited on the bottom, when the weight of carbon which has already been deposited on the stones is added, is so small, both in the cracking and in the Bergius method, that, if the duration of the experiments is long enough, the paraffin wax is entirely converted into oil and gas in both processes.

There is a great difference in the nature of the residues left on the distillation of the oil obtained according to Engler's method. Its specific gravity is always lower in berginization than in cracking, which is a confirmation of corresponding experiments made by Bergius. It appears from the final pressure and also in connection with the gas analysis (percentage of hydrogen) that actually considerable quantities of hydrogen are absorbed in the berginization.⁵⁶

⁵⁵ Brit. Pat. 276,007, convention date Dec. 17, 1925; *Chem. Age* (London), 1927, **17**, 330.

⁵⁶ Waterman and Perquin, *J. Inst. Petr. Tech.*, Sept., 1924, **10**; *Proc. Kon. Akad. van Wetenschappen*, 1923, **26**, 226; *ibid.*, 1924, **27**, 83; *Chimie et Ind.*, May, 1923, *Special No.*

4457. This work was continued and reported in later papers.⁵⁷ The products obtained by heating for various periods were compared. Waterman concludes that the hydrogen used in berginization remains in the gases, but prevents the loss of hydrogen from the residues which occurs in cracking, practically no residue non-volatile below 300° being obtained after treatment for four hours. In the early stages, the proportions of gas and light spirit formed are less when hydrogen is used, but in the later stages they are higher. He also concludes that the presence of hydrogen does not cause the saturation of unsaturated compounds formed, but causes the molecules to break down more regularly than in cracking, and diminishes polymerization and formation of coke.⁵⁸

Probably these conclusions in their entirety should not be applied to hydrogenolysis broadly in view of the results obtained by numerous observers indicative of the substantial absence of polymerization and the complete elimination of carbon or coke. *Hydrogenolysis*, as already pointed out, comprehends a group of reactions fundamentally different from those of ordinary *pyrolysis*.

4458. An elaborate investigation was made of the liquid reaction products obtained by the action of hydrogen on paraffin wax under high pressure at 450° C.⁵⁹ It was found that the gasoline fractions contained large quantities of the successive members of the methane series (up to nonane) and, apparently, about 10 per cent of olefines. Benzene and toluene are present, if at all, in minimal quantities.⁶⁰

4459. Fischer and Schröder had shown that considerable hydrogenation resulted from the treatment of coal with sodium formate and with carbon monoxide, and the result was tentatively attributed to the action of nascent hydrogen. These two experimental methods were applied by Waterman and Kortlandt,⁶¹ the formate method with Mexican asphalt, and the carbon monoxide with paraffin wax.⁶² The results were substantially negative. This was thought to be due to the difference in oxygen content between Fischer's material (brown coal) and the asphalt and paraffin wax: the last two are poor in oxygen. The work was, therefore, repeated with brown coal and paraffin wax (the wax now acting as a "solvent").⁶⁴ Three series of experiments were made, all at about 423° C., in the shaking autoclave. The coal contained 30 per cent moisture. In the first series, no gas was added, the initial pressure was atmospheric, the maximum 80 atmospheres. In the second series, hydrogen was pumped in to a pressure of 7

⁵⁷ (1) Waterman and Kortlandt, *Rec. Trav. chim. Pays-Bas*, 1924, **43**, No. 3 (Mar. 15); (2) Waterman and Blaauw, *ibid.*; (3) Waterman and Perquin, *Proc. Kon. Akad. van Wetenschappen*, 1925, **28**, 286; (4) Waterman and Blaauw, *Rec. Trav. chim. Pays-Bas*, 1926, **45**, No. 3 (Mar. 15).

⁵⁸ *J.S.C.I.*, 1925, 746B; Waterman and Perquin, *loc. cit.* (3).

⁵⁹ Waterman and Blaauw, *loc. cit.* (4).

⁶⁰ See also Waterman and Perquin, *Rec. trav. chim.*, 1920, **46**, 200; *Brit. Chem. Abst.*, 1923, 4B; *Idem.*, *Proc. Kon. Akad. van Wetenschappen*, 1924, **27**, 132; Waterman and Perquin, *J. Inst. Petrol. Technologists*, 1927, **13**, 413. Contribution to the knowledge of berginization and a study on the technical chemical investigation of hydrocarbon mixtures. Part I. Refractometric methods, bromine value and molecular weight determination applied to products of cracking paraffin wax.

⁶¹ See para. 4407 for formate and 4413 for carbon monoxide.

⁶² *Loc. cit.* (1).

⁶³ The carbon monoxide method was also tried with cellulose, paraffin wax serving as a liquid medium. The results were also almost negative. Waterman and Kortlandt, *Rec. Trav. chim. Pays-Bas*, 1924, **43**, 693.

⁶⁴ Dutch Pat. 9757, July 16, 1923.

atmospheres, the maximum pressure attained was about 90 atmospheres. In the third series, carbon monoxide was used, the initial pressure was 19.5 atmospheres, the maximum about 108 atmospheres. The results thus obtained suggest that brown coal, unlike paraffin wax, uses up molecular hydrogen and that the nascent hydrogen obtained from carbon monoxide and water has a still stronger action than molecular hydrogen.

4459A. A comparison of analogous fractions from the vacuum distillation of the products of thermal decomposition of paraffin wax in the presence (berginization) and in the absence (cracking) of hydrogen under high pressure shows that the aniline point of the berginization product is about 20° higher than that of the cracked product, the refractive index of the cracked products is 0.02–0.03 higher, their specific gravity is higher, and the bromine value of the cracked products is much higher, substitution more readily taking place on cracking than on berginization. Comparison with the physical constants of the normal saturated aliphatic hydrocarbons indicate the berginized product to consist possibly of 90 per cent of saturated hydrocarbons, while the cracked product is strongly unsaturated and contains compounds of a cyclic character.⁶⁴

4460. Summary of Results. In experiments on paraffin Waterman and Perquin find that the spirits obtained by cracking and by berginization differ little with respect to distillation curve, for with both types of spirit there are peaks in the curve indicating the presence of pentane, hexane, heptane and octane. There is only 3–4 per cent of the hydrocarbons in the berginized spirit, while there is even less in the cracked spirit. There are still further differences between the two types of spirit.

(1) The berginized fractions and the residues from distillation are relatively stable. Even after twelve to eighteen months the refractionation of the various distillates shows little or no change.

(2) The products of berginization contain olefines, while hexane, heptane and octane constitute about 10 per cent.

(3) The cracked distillates are unsaturated to a far greater extent, they have a higher bromine value, specific gravity, refraction and dispersion, and a lower amine number. The cracked distillates and residues are characterized by their lack of stability; their specific gravity and refraction increase rapidly.

(4) As the boiling-points of similar fractions increase, the differences between berginized and cracked spirits become more marked.

(5) It appears that in the cracked distillates, between the peaks of normal aliphatic hydrocarbons, there are other types of hydrocarbons with a higher refractive dispersion and proportionally lower bromine and aniline values.⁶⁵

4460A. Heating a wax-containing Grozni mazout with hydrogen under 55–265 atmospheres and at 440°–460° for periods of 1.1–2.5 hours yielded 25–34 per cent of benzine (boiling to 150°) and 29–35 per cent of kerosene (boiling point range 150°–300°). The benzine was clear and colorless, and unaffected by fuming sulphuric acid. The kerosene darkened

⁶⁴ Waterman, teNuyl and Perquin, *J. Inst. Petroleum Tech.*, 1929, **15**, 369–371; *Brit. Chem. Abst.*, 1929, 931B.

⁶⁵ *Bull. Soc. Chem. Ind.*, 7th Congr. Ind. Chem., 1927; *J. Inst. Petr. Techn.*, Dec., 1927, 294A.

on keeping, but could be refined by treatment with concentrated sulphuric acid or powdered silica gel. The yields were unaffected by the addition of such catalysts as iron or copper oxide. In only one experiment was any coke formation observed.⁶⁴

4461. Decomposition of Cellulose under Pressure, with and without a Liquid Medium and an Atmosphere of Hydrogen.⁶⁵ Cellulose, in the form of cotton pellets, when heated under pressure at temperatures varying from 225° to 450° C. both in the presence and in the absence of hydrogen, was rapidly decomposed. At 225°, after two hours' heating, 85 per cent of the cellulose was recovered as a black residue resembling coal (carbon 48.9 per cent, hydrogen 6.1 per cent). At 300°, after one hour heating, only 54 per cent of solid residue (carbon 71.0 per cent, hydrogen 5.2 per cent) was obtained, about half the cellulose being converted into carbon dioxide and water, together with a small amount of methane. At 450° a much more profound decomposition took place, the chief products being carbon dioxide, carbon monoxide, water, and methane and homologs, with 37 per cent of solid residue (carbon 85.7, hydrogen 5.0 per cent). The nature and quantity of the reaction products were not greatly affected by the presence of hydrogen, although the amount of hydrocarbons formed was increased. There was a considerable evolution of heat during decomposition. The heat of combustion of the solid residue obtained at 450° was 7832 g.-cal./g., against 4158 g.-cal./g. for the cellulose used. On heating the cellulose in the presence of a liquid medium (Borneo petroleum) an increase in the yield of methane and homologs and a decrease in the amount of solid residue resulted.⁶⁷

4462. Chemical Decomposition of Sphagnum by Pressure Hydrogenation.⁶⁸ Sphagnum moss was treated and converted mostly into oil. Parallel tests were made and material balances obtained. As in the berginization of bituminous coal, oil apparently entirely fluid at first, contained visible colloidal precipitates after several days' standing. The colloids were of asphaltic character. It is considered by Waterman and Perquin important in berginization to keep colloids dispersed by suitable oil media (e.g., Edeleanu-extract). Otherwise, they will be precipitated on the container walls and form coke which is resistant to hydrogenation.

4463. Shatwell, writing in 1924,⁶⁹ and basing his remarks on experiments with gas-oil, held that in berginization, first a cracking process, then hydrogenation took place. He found the products of batch berginization less unsaturated than those of simple cracking and believed that the continuous method of Bergius would lead to further hydrogenation. The conclusions of Shatwell scarcely can be borne out by the author's observations on modern processes of hydrogenolysis. Pyrolytic cracking involves the formation of heavier as well as lighter products, a conversion frequently overlooked in a superficial consideration of the subject of cracking. In other words, starting with a given oil and subjecting it to that form of heat decomposition recognized as pyrolytic cracking, there will be formed, besides gases, liquid products which are lighter and more volatile than the initial oil, together with heavier oils and tars. The reactions of polymerization which form these heavier products are far-reaching. Viewed from one standpoint modern hydrogenolysis may be denominated an orienting reaction tending to establish non-polymerizing conditions or at least serving in large measure to nullify the effect of such conditions. The products of hydro-scission made according to present approved methods normally are almost entirely lighter bodies.

⁶⁴ Ipatiev, Orlov and Bielopolski, *Brennstoff-Chem.*, 1920, 10, 346; *Brit. Chem. Abst.*, 1929, 1004B.

⁶⁵ Waterman and Perquin, *Rec. Trav. chim. Pays-Bas*, 1926, 45, 638.

⁶⁷ *Brit. Chem. Abst.*, 1926, 974B.

⁶⁸ Waterman and Perquin, *Brennstoff-Chem.*, 1928, 9, 57; *Chem. Abst.*, 1928, 22, 2652.

⁶⁹ *J. Inst. Petrol. Techn.*, 1924, 10, 903.

that of the present cost of producing gasoline from natural oils. To those, however, who are apprehensive of a possible rapid exhaustion of our oil resources the opportunity available to convert coal into liquid hydrocarbons is most reassuring. Due attention is being given by petroleum oil companies to this phase of the fuel situation, since therein they perceive resides the means to carry on after depletion of natural oil supplies has raised oil-fuel values to considerably higher levels. The process of liquefaction of coal by hydrogen, viewed only a few years ago with scepticism, now is generally accepted as a desirable provision which will assure, even into the far-distant future, an abundance of liquid fuels.

4468. In the course of a discussion on the work done at the Mines Research Laboratory (Birmingham, England),⁷³ it seemed to be the general opinion that most of the gasoline, etc., produced by berginization in Germany was obtained, not directly from coal, but from low-temperature tars.

4469. A series of articles published in 1926⁷⁴ by Nielsen, advocates the most efficient method of converting coal to oil as: (a) low-temperature carbonization in the Laing and Nielsen retort, and (b) using the coke as a source of water-gas and converting the latter into Synthol.

4470. In this connection the following summary of the position, by Brunschwig⁷⁵ is of interest. The possibilities of obtaining light oil products from the phenolic fractions of the primary tar from low-temperature coal carbonization include Fischer's process for hydrogenating at 700° and atmospheric pressure with a catalyst, producing aromatics and paraffins; the several methods of hydrogenating under pressure in presence of suitable catalysts; decomposition under pressure of hydrogen as tried at the Institute Technique de Chimie de Budapest; cracking by the Dubbs process; the Prud'homme patents by which lignite-tar vapors are treated before condensing with a desulphurizing agent and then by a series of catalyzers which convert them partially into fuels; the Compagnie de Noeux and the Kling-Florentin patents which relate to cracking under pressure of hydrogen in presence of aluminum chloride catalysts; and the innumerable patents of the I. G. Farbenindustrie for hydrogenating lignite or the phenolic fractions of coal tars under pressure in the presence of such catalyzers as cobalt or manganese sulphide, insensitive to the action of sulphur. For successful commercial exploitation the following conditions are important:

A. The avoidance of equipment whose output is too small in relation to the weight and the space occupied.

B. Careful study of the mode of handling and the progression of the fuel to the interior of the apparatus.

C. No exposure of the tar vapors to cracking by contact with the semi-coke or with hot walls.

D. As an economic generalization, it is essential to choose such conditions and such a formula of low-temperature carbonization that the semi-coke has a distinctly higher value than the starting material. The operation of low-temperature carbonization and that of treating the tar present too great hazards to be undertaken without a sufficient margin of safety based upon the valorization of the solid fuel.⁷⁶

Of the methods thus considered by Brunschwig the most outstanding probably is the development by I. G. Farbenindustrie of catalyzers which, as stated, are insensitive to the action of sulphur. Catalysts which are sulphur resistant are fast reaching a position of great importance in hydrogenolysis.

4471. Coke-oven Tars: Berginization. Bruylants⁷⁷ successfully berginized the residues of coke-oven tars, i.e., the part boiling above 230° C. But the high

⁷³ *Chem. Age* (London), 1929, **20**, 25.

⁷⁴ *Gas J.*, 1926, **174**, 591, 650, 732; *Brit. Chem. Abst.*, **1926**, 698B.

⁷⁵ *Chal. et Ind.*, Mar., 1928, 143.

⁷⁶ *Univ. Oil Prod. Co. Bull.*, May 2, 1928.

⁷⁷ *Bull. Soc. Chim. Belg.*, 1923, **33**, 194.

temperature of 478° C. was required. Three hours' treatment resulted in the absorption of a considerable quantity of hydrogen and in the production of a black, mobile liquid smelling strongly of ammonia. The fraction boiling below 330° C. was more than doubled. The fraction distilling below 170° C. contained 11.26 per cent of hydrogen, and its chemical composition corresponded with that of high-class motor gasoline.

4472. Tar Oils: Experimental Berginization. Erdley⁷⁸ subjected tar oils to berginization at different pressures. Oils tested were: generator tars (a) raw boiling 92°–350°, 4 per cent residue; (b) phenol-poor boiling 90°–350°, 3.1 per cent residue; (c) phenol-free boiling 190°–350°, 3.7 per cent residue; primary tars (a) raw boiling 190°–350°, 2 per cent residue; (b) phenol-poor boiling 185°–350°, residue 4.7 per cent. These oils had been distilled to pitch and separated therefrom previously. A Texas gas-oil (boiling 283°–350°, residue 28.2 per cent) was included for comparison. The treatment was in a rotating steel bomb with and without initial pressure of hydrogen. In all cases hydrogen pressure gave the best yields. Optimum conditions for gas-oil were 75 atmospheres hydrogen, heating time five to fifteen minutes at 475°, the yield being 33 per cent benzine boiling under 200°. Optimum conditions for all tars were the same: viz., 75 atmospheres hydrogen, 15 minutes heating at 450°. Yields of benzine boiling under 200 were: generator tar oils (phenol-poor) 30 per cent (raw) 24.5 per cent; primary tar oils 23–25 per cent. Benzine from gas-oil did not darken on standing; that from the tars did. Color-stable tar benzine was obtained by refining, but the refining loss was 20–25 per cent.⁷⁹

4473. Berginization of Tar. Berginized tar yielded light oils which, after removal of acidic and basic constituents, were divisible into three fractions boiling between 70° and 170° in which benzene, toluene, and xylene respectively could be identified. The neutral oils boiling below 70° appeared to be a mixture of aliphatic or cyclic saturated hydrocarbons with small quantities of unsaturated and aromatic hydrocarbons. Low-boiling aliphatic or cyclic saturated hydrocarbons (perhaps also cyclohexane) were isolated in very small quantities. Berginization of tar has the effect of increasing the content of low-boiling phenols and bases at the expense of the higher homologs. Aniline was isolated in one experiment. De-alkylation appears to take place, and a large quantity of methane hydrocarbons is found in the gases finally leaving the autoclave. The nature of the final products, i.e., the extent of de-alkylation and decomposition, will depend on the temperatures and pressures employed.⁸⁰

4474. Combined Carbonization and Berginization.⁸¹ Coal is carbonized to give coke, tar, ammonia, a gaseous fraction poor in hydrogen and of high calorific value, and a gaseous fraction rich in hydrogen. The tar is mixed with a further supply of coal and is hydrogenated at an elevated temperature and under a high pressure, the gaseous fraction rich in hydrogen being utilized in this process, together with hydrogen obtained from water-gas made from the coke. The hydrogenation yields oil, ammonia, and gas of high calorific value, which is combined with the gaseous fraction poor in hydrogen and some water-gas to give city gas.⁸² This may be regarded, from one point of view, as an attempt at an indirect solution of the hydrogen problem in berginization.

4475. Hydrogenation of Carbonization Products.⁸³ In a method of hydrogenating the middle fractions from low-temperature carbonization of coal the fractions boiling between 250° C. and 350° C. are passed with hydrogen at a high

⁷⁸ *Brennstoff-Chem.*, 1926, 7, 359.

⁷⁹ *Chem. Abstr.*, 1927, 21, 1535.

⁸⁰ Rheinfelder, *Mitt. Schles. Kohlenforschungsinstit. Kaiser-Wilhelm-Ges.*, 1925, 3, 34; *Chem. Zentr.*, 1926, II, 510; *Brit. Chem. Abstr.*, 1926, 780B.

⁸¹ Bergius, U. S. Pat. 1,669,439, May 15, 1928.

⁸² *Brit. Chem. Abstr.*, 1928, 469B.

⁸³ I. G. Brit. Pat. 273,337, June 26, 1926.

temperature and under at least 50 atmospheres pressure over porous charcoal active silica, or hydrosilicates. Liquid hydrocarbons of low boiling-points are obtained.⁸⁴

4476. Feige ⁸⁵ treats low-temperature tar by hydrogenating it with hydrogen and water-gas obtained, in a series of operations, from the coke of the original coal from which the tar was made.

4477. Hugel ⁸⁶ affirmed the suitability of simple, i.e., non-catalytic berginization for the hydrogenation of coal-tar and described, in some detail, his own results with a coke-oven tar.

4478. Products of Berginizing Lignite together with Coal-tar.⁸⁷ A mixture of 100 kg. of Italian lignite with 67 kg. of topped coal tar and 4 kg. of "Lux" material was berginized in a 50-liter bomb by the continuous method, with the addition of 5 kg. of hydrogen. The finely ground lignite was mixed with the tar to form a paste. The lignite contained 13.8 per cent of water, 8.45 per cent of ash, and 0.8 per cent of sulphur. Hydrogenation took place at 470° under a pressure of 140–150 atmospheres. The expansion gases were freed from benzene by activated charcoal, yielding 8 kg. of benzene. Twenty kilograms of gas were formed and 139 kg. of "runnings," and the loss was 9 per cent. The benzene was water-white, had an odor of petroleum benzene, and sp. gr. 0.7303. 84.6 per cent distilled over from 50° to 120°, and the benzene was easily refined. The relation between boiling-point range and specific gravity corresponded to that of American benzene. The lower fraction obtained by distilling the "runnings" had sp. gr. 0.990 and contained 12.5 per cent of phenols, being similar to a low-temperature tar oil. The wax content was 1 per cent to 1.5 per cent. The residue was very viscous, and on re-distilling 47 per cent of hard asphalt remained, indicating a total asphalt content of about 60 per cent, but the ash content was small. A third fraction of the "runnings" consisted of water (29.5 kg.) containing 7.83 g. of ammonia per liter. This only corresponded to 19 per cent of the total nitrogen present in the raw material, the rest having escaped as ammonia in the expansion gases.⁸⁸

4479. Low-temperature Tar Oil: Berginization.⁸⁹ A neutral oil fraction of Fushun tar, of boiling range about 200° to 350°, has been hydrogenated (berginized) in a 600-cc. autoclave under various conditions of temperature and pressure. Above a definite temperature, about 450°, decomposition of the oil occurs with separation of free carbon. Hydrogenation proceeds most favorably just below this temperature; the initial pressure of the hydrogen should be at least 75 atmospheres. It is, however, impossible to hydrogenate the oil completely, the iodine value of the product still amounting to 65 per cent (approximate) of that of the original oil. In the presence of nickel oxide the hydrogenation is much more complete, and it is possible to bring the iodine value down to 12 per cent of the original. Ferric oxide has a slight favorable effect, and the addition of zinc oxide also lowers the iodine value of the product. Copper and magnesium oxides are without action, while the addition of alumina appears to accelerate the decomposition of the oil.⁹⁰

4480. Experiments carried out at H. M. Fuel Research Station on the production of low-temperature tar oils suffice to indicate that on a large scale the yields of tar are not much greater than 16.5 gal. per ton of coal, and if 50 million tons of coal were carbonized only 150 million gallons of motor spirit and 550 million gallons of tar oils would be available—much less than British require-

⁸⁴ *Chem. Age* (London), 1927, **17**, 221.

⁸⁵ *Brit. Pat.* 274,465, July 16, 1926; *Chem. Age* (London), 1927, **17**, 291.

⁸⁶ *Second Internat. Conf. Bitum. Coal*, 1928. *Idem*, *Chimie et industrie*, 1929, Spec. No. 128 (hydrogenation of pitch); *Chem. Abst.*, 1929, **23**, 3561.

⁸⁷ Laszlo, *Petroleum*, 1926, **23**, 421.

⁸⁸ *Brit. Chem. Abst.*, 1926, 523B.

⁸⁹ Tashiro, *J. Fuel Soc.*, Japan, 1928, **7**, 67.

⁹⁰ *Brit. Chem. Abst.*, 1928, 776B.

ments. The Bergius process offers technically 100-130 gal. of oils per ton of coal or up to 60 per cent by weight of suitable coals.⁹¹

4481. Coke obtained from Sharlston Wallsend coal, containing 1.3 per cent of ash, at 800°C. for six hours, was heated for one hour at different temperatures in hydrogen, carbon monoxide, methane, and ethylene, and changes in the reactivity of the coke with carbon dioxide were investigated. Heating in hydrogen or carbon monoxide at 900° led to slight loss of activity, while the effects with methane were greater; the influence of ethylene was much more pronounced and appeared at lower temperatures.⁹²

4482. Pertierra⁹³ determined the plasticity of a coal before and after Bergius hydrogenation. He found that the initial temperature of plasticity was reduced, and that of solidification raised by such treatment.

⁹¹ King, *J.S.C.I.*, 1927, **46**, 181T; *Brit. Chem. Abst.*, 1927, 641B.

⁹² Sutcliffe and Cobb, *Gas J.*, 1928, **183**, 948; *Brit. Chem. Abst.*, 1928, 556B.

⁹³ *Anales soc. espan. fis. quim (tecnica)*, 1929, **27**, 191-4; *Chem. Abst.*, 1930, 484.

CHAPTER XLV

HYDROGENATION OF COAL AND RELATED HYDROCARBONS

II

HIGH-PRESSURE HYDROGENATION WITH ADDED CATALYSTS (HYDROGENOLYSIS)

4500. Primarily, berginization was typically carried out without *added* catalysts, though, in practice, Bergius seems from the first to have added ferric oxide to his mixture. It would, however, be rash to affirm that even simple berginization was an operation independent of catalysis, in view of the complex nature of powdered coal with its carbon, its sulphides, its nitrogen compounds and its mineral constituents, all potential catalysts. In fact, the negative results of attempts to berginize approximately pure substances, such as cellulose, without catalysts, and the poor results obtained with ferric oxide only, lend support to the surmise that possibly coal contains a catalyst for berginization.¹ For this and for reasons of convenience we shall use "hydrogenolysis" for all processes in which fuel material is treated with hydrogen at high pressures and high temperatures, whether catalyst is added or not. Another general term frequently used, which requires no explanation, is "destructive hydrogenation."

4501. In a discussion of results obtained in the hydrogenolysis of coal at Birmingham University to which reference has already been made,² no one seems to have expressed any doubt that the use of catalysts improved the yield. Graham, the reporter, spoke of work with catalysts, but, apparently, without mentioning the quantity of catalysts used. The results were a decrease in the unconverted residue from 18.2 per cent without a catalyst to 9.6 per cent with nickel oxide, to 7.2 per cent with nickel oxalate, and to 5.5 per cent with ammonium molybdate, with a corresponding increase in the yield of oil. Ormandy put forward the view that the iron oxide used by Bergius as a desulphurizing agent had always been regarded as having, also, catalytic functions, although in a patent Bergius said that he did not work with a catalyst.

4502. Friess,³ limiting berginization to the process by which coal is hydrogenated at high temperatures and pressures with no added catalyst except oxide

¹ Brit. Pat. 302,912, Dec. 23, 1927, to Ges. für Teerverwertung describes the hydrogenation of naphthalene and benzene using as *catalyst* the residue from the berginization of coal. Hlavica (*Brennstoff-Chem.*, 1929, **10**, 201; *Brit. Chem. Abst.*, 1929, 666B) finds that the iron-containing constituents of coal have an important catalytic effect in promoting hydrogenation, especially of bituminous coal.

² Para. 4441.

³ *La Rev. Petrol.*, July 28, 1928, 1050.

of iron, held that this is sure to give way to frankly catalytic methods. Particularly does he feel that this is true where it is desired to control the nature of the product. Results obtained in the operation on a semi-commercial scale in the hydrogenolysis of petroleum oil tend to confirm the validity of the foregoing observation of Friess. Undoubtedly in this phase of the petroleum oil industry catalysts are destined to become of great importance. The observation holds good both for a moderate or mild degree of treatment with hydrogen such as hydrofining, as well as more drastic hydrogenolysis.

4503. The studies of Waterman and Perquin (1925), Dunkel and Heim (1925), Kling and Florentin (1926), Spilker and Zerbe (1926), Hugel and Friess, and Fricke and Spilker (1925) upon the mechanism of hydrogenation at least have shown that several processes may go on in hydrogenation. (1) Hydrogen may be simply added to the hydrocarbon molecule. (2) Hydrogen may add itself to the molecule which then dissociates, each fragment adding on hydrogen. (3) The original molecule may be variously dissociated. (4) In either of the two latter cases the separate portions may again associate themselves into new molecules which are or are not hydrogenated. The course of the reaction is influenced favorably by pressure between maximum and minimum limits. The temperature is the most important factor. High temperature is in general unfavorable to hydrogenation. The optimum for high yield is about 450° for complex mixtures like the tars, pitches, coals, etc. With pitch from coal tar, fixation of hydrogen begins at 300°, is appreciable at 350°; then cracking prevails with the residues adding on hydrogen, for at 480° the fixation of hydrogen becomes very important. The cyclic structure of the pure aromatics is opposed to one or other of these processes. Benzene and phenol are unchanged, naphthalene is changed but little if at all, anthracene is hydrogenated with or without decomposition. Bergius' claim that his use of ferric oxide is an aid to hydrogenation has little point because, while it removes sulphur, there is no catalyst present to be poisoned by the sulphur. The final products, however, are improved by the removal of sulphur.

4504. "Destructive hydrogenation" is a term justified by the facts. Ipatiev (1925) treated naphthalene under hydrogen pressure at 450° with reduced nickel and alumina and obtained among the products 30 per cent of benzene hydrocarbons, showing that the tetra-hydrogen nucleus of the naphthalene must have been ruptured.

4505. It is clear that chemical reactions so complicated as those taking place in an autoclave cannot be controlled by the sole factor of temperature; and, seemingly, that in order to cause the reaction to go in any desired direction the appropriate catalysts must be used. As an instance of producing a specific product pitch (from coal tar) can be made to yield highly viscous lubricants by using catalysts not easily poisoned by sulphur. In other cases cracking or dehydration may be the important objective. Friess predicts that the Bergius process of hydrogenating at high temperature and high pressure will be displaced by processes using catalysts.⁴

4506. In 1925, Fierz-David,⁵ of Zurich, published the result of experiments on the liquefaction of wood and cellulose. The experimental part of this paper dealt with the attempted hydrogenation under berginization conditions of pressure and temperature of starch, lignin and other substances. The results both with and without catalysts (the best of these being nickel) were negative as regards any evidence of hydrogenation: all the hydrogen was recovered in the gas issuing from the apparatus. The product contained a large percentage of oxygenated compounds.

⁴ *Univ. Oil Prod. Co. Bull.*, Aug. 22, 1928.

⁵ *J.S.C.I.*, 1925, **44**, 942.

4507. Fierz-David shows a good deal of scepticism as to the results claimed for berginization. It is, however, to be noted that he did not use a "solvent," and that his apparatus was stationary, so that his work is not comparable with that of Bergius, which somewhat discounted the weight of his criticisms. At the present day the claims of Bergius have been amply substantiated by results obtained by independent workers.⁶

4508. Under the stimulus of competition from synthetic methanol, research workers are busy with the problem of rendering more efficient the old-established wood distillation process. Frolich, Spalding and Bacon⁷ distilled birch wood with and without catalysts, under hydrogen pressure (200 atmospheres), and under pressure of the gases evolved—"autogenous pressure"—(90–300 atmospheres). Comparison runs were made with cellulox (sulphite pulp) under hydrogen pressure (200 atmospheres) and under nitrogen pressure (200 atmospheres), and with wood under atmospheric pressure. Pressure alone, whether of hydrogen or of autogenous gases, increases the production of methanol. The catalysts used (zinc-chromium oxides introduced as nitrates; copper, zinc and aluminum oxides, introduced as acetates; nickel oxide, introduced as acetate; sodium carbonate) either reduced the methanol yield (atmospheric pressure) or barely increased it (high pressure). With the nickel catalyst at 200 atmospheres pressure (of hydrogen in the case of wood, of hydrogen or of nitrogen in the case of cellulose) almost complete liquefaction and gasification resulted. An oily liquid, 40 per cent boiling below 225° C., was obtained. Forty-three per cent of this fraction was phenolic, 26 per cent unsaturated and 31 per cent saturated hydrocarbons.

4509. Bowen, Shatwell and Nash⁸ worked on the berginization of cellulose, using a batch method with a rotating autoclave. The first experiments were made without catalyst. There was a rise of pressure to the end and the analysis of the residual gases showed no unequivocal evidence of absorption of hydrogen. When a nickel catalyst was used not only did a fall of pressure occur, but analysis showed a considerable increase in carbon dioxide, and some decrease in hydrogen. The percentage weight of hydrogen absorbed calculated on the ash-free dry cellulose was in one experiment 4 and in the other 3. Practically the whole of the cellulose had been converted into liquid and gas. Other catalysts used were ferric vanadate and ammonium vanadate. These two catalysts had very little action: there was more absorption of hydrogen than in the absence of catalysts, but far less than with nickel. Comparing the products with those obtained from British coals by these workers and Graham⁹ it is suggested that there is a chemical basis or nucleus, common to cellulose and the coals. The fact that a catalyst is necessary for the berginization of cellulose is not fatal to this theory, because, as we have already said, some constituent of coal may act as a catalyst.

⁶ E.g., Kling, *Chaleur et Industrie*, Spec. No., 53 (Dec. 1, 1924).

⁷ *Ind. Eng. Chem.*, 1928, **20**, 36.

⁸ Bowen, Shatwell and Nash, *J.S.C.I.*, 1925, **44**, 507T and 526T.

⁹ *Fuel*, 1925, **4**, 25, 75, 127, 252.

4510. Bowen and Nash¹⁰ in further experiments on the thermal decomposition of cellulose and lignin in presence of catalysts under high hydrogen pressure, like Fierz-David, did not use a solvent. Also, like him, they obtained (for a static or bomb experiment) thorough permeation of the mass by mixing the finely divided substance to be hydrogenated, intimately with the catalyst, in the moist state and then drying the mixture. The catalyst used was (in its original condition) a mixture of aluminum hydroxide 10 parts and nickel oxide 5 parts (in the form of oxalate or hydroxide). This was moistened and worked into a paste with the cellulose, etc., and dried at 110° C. The treatment was carried out in a rotating autoclave. This movement of the mass during treatment probably contributed to the success of the work. Nevertheless, Bowen and Nash are of opinion that completion of the hydrogenation was prevented by the deposit of carbon on the catalyst mass. It may be that in similar experiments, where a solvent is objectionable, indifferent heavy abrasive masses can be introduced with advantage to maintain clean catalyst surfaces.

4511. Their conclusions are: (1) Catalysts assist in the formation of liquid and gaseous products from cellulose and lignin by thermal decomposition under hydrogen pressure, but fully saturated oils are not obtained under the experimental conditions described owing, in all probability, to the deposition of small quantities of coke on the surface of the catalyst. (2) The oils from cellulose and lignin are comparable as regards main constituents; the lignin oil is characterized by a greater phenol content, and also by the presence of phenol-soluble substances. (3) Cellulose 400° coke is capable of hydrogenation and yields an oil with relatively low proportion of volatile constituents. Phenols are also formed to the extent of 1.62 per cent. (4) The volatile neutral oil fractions from cellulose, cellulose coke, and lignin were found to have an appreciable hydrocarbon content, the saturated portion of which possessed a paraffinic odor in two former cases.

4512. The same two workers¹¹ employed a similar technique in catalytic berginization of coal (Arley coal). An addition to the former technique was the placing of small steel cylinders in the autoclave with the charge, thus effecting better stirring. The percentage conversion was good, but not as high as that obtained with the same kind of coal when a solvent (phenol) was used.¹² Their results may be summarized as follows:

(1) Nickel and iron oxides have a marked catalytic influence on the thermal decomposition of Arley coal under hydrogen pressure. Under comparable conditions, up to 45.64 per cent of oil products was obtained with nickel oxide catalyst and up to 30.95 per cent with iron oxide, all experiments in absence of liquid media. (2) The proportion of phenols and bases in the oils obtained with these two oxides was approximately the same, irrespective of the oil yield, and mean values were 9.21 per cent phenols and 6.41 per cent bases. (3) The light fractions obtained were not fully saturated and their amount depended on the maximum temperature employed.

4513. Hydrogenation of Coal: Comparison of Catalysts. Hlavica¹³ subjected coals to hydrogenation by heating under hydrogen pressure with catalysts, in a rotating autoclave, steel balls being used to agitate and grind the coal. No oil was added. Bergius' ferric oxide catalyst was tried as also were the oxides and chlorides of aluminum, calcium, cobalt, copper, manganese, nickel, tin, and zinc and sodium and potassium hydroxides. Zinc, nickel and cobalt chlorides and oxides and cuprous chloride as catalysts, compared with iron oxide, doubled the yield, reduced the reaction period by one-third and gave a better product. The use of catalysts did not permit of lowering either the temperature or the hydrogen pressure. Hydrogen could not be replaced by nitrogen. The process has three stages (1) a stage of rapid hydrogen absorption (300°–400° C.); water is formed and an asphaltic mass; (2) a stage of liquefaction during which the absorption of the gas is slowed up; (3) a dissociating stage in which are produced gasolines, permanent gases and other products of molecular cleavage, controlled by the presence of hydrogen under pressure.

4513A. Light hydrocarbons are produced from complex products such as tars from low-temperature distillation of coal by the action of heat, hydrogen under high pressure, dehydrating catalysts such as those described in French Patent 608,560, substitution catalysts (defined in French Patent 607,155) and hydrogenating catalysts composed either of reduced metal (iron, cobalt, etc.) or unstable derivatives such as suboxides, sulphides, nitrites,

¹⁰ *Fuel*, 1926, 5, 138.

¹¹ Bowen and Nash, *Fuel*, 1926, 5, 361.

¹² Shatwell and Bowen, *Fuel*, 1925, 4, 252.

¹³ *Brennstoff-Chem.*, 1928, July 15, 229. *Chem. Abst.*, 1929, 23, 2806. *Idem*, *Brennstoff-Chem.*, 1929, 201.

etc. of multivalent metals (tungsten, vanadium, uranium, manganese, iron, chromium, etc.)^{13a}.

4514. Hydrogenating Solid Fuel to Produce Liquid Hydrocarbons.¹⁴ The finely divided solid (e.g., lignite) either alone or, preferably, mixed with oil, is fed in counter-current against a stream of hydrogen, with or without catalysts, at a temperature of 450° C. and a pressure of 200 atmospheres. Suitable catalysts are pumice, fireclay, zinc oxide or other metal oxides not easily reduced. The gaseous products are led, without reduction of pressure over calcium carbonate at 500°–550° C., then through a heat exchanger to a condenser.¹⁵

4515. Nitrogen Compounds as Catalysts in Manufacture of Hydrocarbons by Hydrogenation of Coal, Bitumen, etc.¹⁶ The raw materials are coal and other solid carbonaceous material, distillation or extraction products of coal, mineral oil or bitumen, conversion or hydrogenation products of coal and bitumen. The raw materials are treated at high temperatures, e.g., 500° C. and at pressures above 50 atmospheres, e.g., 200 atmospheres, with hydrogen or hydrogen-yielding gases. Nitrogen compounds, with or without other catalysts, are introduced. By admitting steam, hydrogen may be generated from the coal, etc., or from carbon monoxide. In the case of carbon monoxide the gases must be introduced in a stream.

4516. When ammonia is used with mineral oils or bitumen some other nitrogenous catalyst is necessary, e.g., silicon nitride.¹⁷ Other compounds mentioned are ammonium sulphide, titanium nitride. Inert supports may be used, also auxiliary catalysts such as iron or cobalt. Instead of hydrogen, water-gas, hydrogen sulphide, methane, etc., may be used as source of hydrogen (247,582).

4517. 247,583 specifies the use of molybdenum compounds as catalysts, e.g., molybdic acid, ammonium molybdate or sulphide of molybdenum, with or without ammonia, iron, cobalt, zinc oxide, magnesia, activated carbon, coke, silica, aluminum hydroxide, calcium carbonate or clay. 247,584 specifies sulphides of the iron group, or sulphates, or sulphites or other suitable sulphur compounds. 247,585 deals with the hydrogenation of crude cresylic acid or other distillates, residues or conversion products from coal or similar materials, in the presence of sulphides of cobalt, nickel, manganese, zinc or aluminum. 247,586 specifies a process for hydrogenating crude cresols, brown coal wax, cumaron resins and the like in presence of molybdenum compounds. 247,587 specifies generally similar processes in which ammonia or other suitable nitrogen compounds are used instead of molybdenum compounds.¹⁸

4518. Reference to 247,583 (preceding paragraph) is made in British Patent 274,401 (Mar. 8, 1926) to the same patentees. The process is here applied to conversion products of mineral oils and bitumens, e.g., cracked products, acid sludge or hydrogenation products of bitumen.¹⁹

4518A. Dunstan^{19a} states that zinc oxide, barium peroxide, sodamide and tungstic acid do not function as catalysts. However, molybdic oxide and pentamine cobaltic chloride act as energetic hydrogenation catalysts.

4519. Hydrogenation with or without Catalysts: Circulation. In the production of lighter hydrocarbons by treating coals, tars, mineral oils, asphaltic materials and other carbonaceous bodies at elevated temperatures and pressures with hydrogen or gases containing or giving rise to hydrogen, the materials are treated in a gaseous or finely divided liquid or solid state. Catalysts, for instance tungsten or nickel, may be added. The hydrogen may be circulated for reuse after addition of water vapor, fresh hydrogen, or both. Carbonaceous material insufficiently converted may be circulated for further treatment, slag and residue being removed en route without loss of pressure; or it may be passed through a series of reaction vessels. . . . In an example, a mixture of 2 tons of mineral oil and 1 ton of lignite containing 40 per cent of water is introduced as a fine mist and at 200 atmospheres' pressure into a reac-

^{13a} Florentin and Kling, French Pat. 659,462, Dec. 15, 1927; *Chem. Abst.*, **1929**, 5306.

¹⁴ Brit. Pat. 249,156, Mar. 14, 1925, an I. G. patent.

¹⁵ *Chem. Abst.*, 1927, **21**, 1002. Can. Pat. 282,876, Aug. 28, 1928, to Krauch and Pier (assigned to the I. G.) seems to cover the general case of berginization with catalysts; *Chem. Abst.*, 1928, **22**, 4234.

¹⁶ Brit. Pats. 247,582, 247,587, 249,493, 250,948, 272,829, 272,834, 272,835, 273,228 to I. G. Farbenind. A.-G.

¹⁷ *Brit. Chem. Abst.*, 1927, 595B.

¹⁸ *Chem. Abst.*, 1927, **21**, 643.

¹⁹ *Chem. Abst.*, 1928, **22**, 2048.

^{19a} *Proc. 2d Internat. conference Bituminous Coal*, 1928, **1**, 210–31; *Chem. Abst.*, **1930**, 712.

tion vessel and reacted upon at 450° C. (842° F.) with a mixture of hydrogen and nitrogen. No coking occurs.²⁰

4520. Catalysts,²¹ for use in berginization, may be composed of difficultly reduced oxides (or the corresponding carbonates) of metals from the 3rd to the 5th group of the periodic system, e.g., alumina, rare earths, difficultly reduced oxides of the 4th group, or oxides or carbonates of vanadium. Metals of the 8th group, such as iron may be present. These catalysts are said to be resistant to poisons.²²

4521. Other catalysts consisting of oxides or carbonates of lithium, magnesium and zinc may be used.²³

4522. Again, catalysts consisting of compounds of lead, cadmium, bismuth, or tin, with or without difficultly reducible oxides or carbonates and with or without metals of the 8th group are available.²⁴

4523. Catalysts may be composed of oxide or carbonate of uranium, with or without 8th group metals.²⁵

4523A. A Badische proposal relates to the use of nickel chromate or nickel borate as hydrogenation catalysts.^{25a}

4524. Coal, tar, bitumen, etc., may be exposed in a thin layer on a screw, or corrugated band-conveyer, to hydrogen at 450°–475° C. under 200 atmospheres pressure in presence of molybdic acid catalyst extended on magnesia or diatomaceous earth.²⁶

4525. Another method is a two-stage or double treatment. The paste of coal, tar, etc., is heated in presence of metals (or oxides) of the 3rd to 8th groups and of hydrogen; the vapors are then superheated and passed again over the catalyst, with hydrogen. The material is passed into the lower part of a vertical retort at 420° C. and hydrogen is passed in at 200 atmospheres. The vapors pass into the upper part of the retort at 480° C.²⁷

4526. Catalysts may consist of elements of groups 4–8 of the periodic system, together with other elements from groups 2–7, or with copper or gold. An example given is molybdic acid and magnesia, copper or aluminum hydroxide. Thus crude mineral oil mixed with ground alderwood charcoal as a catalyst is treated with excess of hydrogen under 200 atmospheres at 450° C. in a vessel lined with chromium nickel. The vapors of the 50–60 per cent middle oils produced are passed with hydrogen at 200 atmospheres and 460° C. over a catalyst of molybdic acid and 10 per cent chromium oxide. The condensed product contains 90 per cent benzine.²⁸

4526A. Low boiling-point hydrocarbons are obtained from carbonaceous materials such as coals, tars or mineral oils by heating to about 450° in the presence of catalysts comprising oxides of the metals or metalloids of groups 3 to 7 deposited in small quantities on metals such as aluminum, silver, manganese, chromium or chromium-nickel alloy. The reaction is preferably effected under high pressure (suitably 200 atmospheres) in the presence of hydrogen or gases containing hydrogen. Compounds of cobalt, ruthenium, platinum, gold and cadmium also may be used as catalysts. A somewhat similar process is proposed for the dehydrogenation of oils, tars and hydrocarbons and their conversion into aromatic compounds.^{28a}

4527. Carbides, active carbon, or metalloids (such as boron, silicon, phosphorus, arsenic,

²⁰ Brit. Pat. 256,965, Aug. 14, 1925, to I. G. Farbenind. A.-G.

²¹ Brit. Pat. 285,923, Sept. 10, 1925, to I. G.

²² *Chem. Age* (London), 1928, 18, 416.

²³ *Ibid.*, Brit. Pat. 286,678, Sept. 10, 1925, to I. G.

²⁴ *Ibid.*, Brit. Pat. 286,679, Sept. 10, 1925, to I. G.

²⁵ *Ibid.*, Brit. Pat. 286,680, Sept. 10, 1925, to I. G.; Brit. Pat. 286,681 covers the use of oxide and carbonate of manganese.

^{25a} Ger. Pat., 362,143, Oct. 23, 1922, to B.A.S.F. See also Swedish Pat., 39,902, May 4, 1914.

²⁶ Brit. Pat. 272,190 (convention date June 1, 1926) by the I. G.

²⁷ Brit. Pat. 272,194 (convention date June 1, 1926), by the I. G.

²⁸ *Chem. Age* (London), 1927, 17, 352; Brit. Pat. application, 275,663 (convention date, Aug. 7, 1926). The I. G. British patents 293,719 and 293,720 (convention date, Aug. 7, 1926) are additions to 275,663. 293,719 claims as catalysts for the berginization of coal a mixture of elements of the 4th–8th group with small proportions of elements of the 4th–7th group. Molybdic acid with 10 per cent of chromium oxide is given as an example. 293,720 describes a catalyst which is a mixture of elements of the 4th–8th groups with copper or gold or their compounds. *Chem. Age* (London), 1928, 19, 243.

^{28a} I. G. Farbenind. A.-G., Brit. Pat., 307,946, Sept. 12, 1927; *Chem. Abst.*, 1930, 234.

selenium, tellurium), or halogens are included as catalysts. Phosphoric or similar acids may be used, and also silicon carbides, borides, active silica, etc. In example, crude mineral oil is mixed with aluminum phosphate and treated with a large excess of hydrogen at 420° C. and 200 atmospheres pressure. The middle oil vapors are again treated with a large excess hydrogen in presence of alderwood charcoal impregnated with phosphoric acid. The product contains 80–90 per cent of low-boiling hydrocarbons.²⁹

4527A. Carbonaceous materials are heated with hydrogen in the presence of catalysts such as calcium, iron-tungsten, or nickel carbides in an autoclave at 460° and 45 atmospheres.^{29a}

4528. Tin, lead or noble metals may be used on supports of magnesia, magnesite, or chromium oxide, e.g., ruthenium, palladium, platinum, gold, lead, or tin on magnesia or magnesite, and platinum or gold on chromium oxide. Methane or water vapor may be employed instead of hydrogen.³⁰

4529. Catalysts for hydrogenolysis³¹ are described which are composed of silver, copper, zinc or cadmium with boron, aluminum, silicon, titanium, vanadium, tantalum, chromium, molybdenum, tungsten, or cobalt. The member from the first group must not constitute more than 10 per cent of the mixture. The example given is the treatment of cresylic acid.³²

4530. Reference is made to the foregoing patent in Brit. Pat. 300,703, Aug. 11, 1927, to Johnson (I. G. Farbenind., A.-G.), in which is described a catalyst composed of: a mixture of copper and zinc (or cadmium) 10 per cent; boron, aluminum, silicon, vanadium, etc., or their compounds 90 per cent. The catalyst can be used for the hydrogenolysis of coal, etc.

4531. (a) Solid carbonaceous materials are treated at an elevated temperature and under at least 50 atmospheres pressure with hydrogen or reducing gases containing combined hydrogen, sulphur compounds (e.g., the sulphides of the heavy metals, especially of the iron group) being admixed as catalysts. (b) Instead of solid carbonaceous material distilled or extracted derivatives thereof are used as raw material. The hydrogenating gases may be used in the form of a stream. (c) In using a stream of gases the process can be rendered continuous. (d) The products of destructive hydrogenation of solid carbonaceous materials and products distilled or extracted therefrom, e.g., cumaron resins and waxes from lignite, serve as raw material.³³

4532. Halogen Compounds as Hydrogenation Catalysts.³⁴ Coal, coal products and hydrocarbons are hydrogenated with catalysts consisting of halogen compounds (not containing iodine) such as occur in the potash industry. For example, naphthalene at 470° C. and 100 atmospheres hydrogen pressure in presence of ammonium chloride, yields 70 per cent of liquid products.³⁵

4533. Iodine Catalyst in Coal, etc., Hydrogenation.³⁶ Spilker and others, deal with hydrogenation of coal, tar, pitch, etc., in the presence of iodine or of an iodine compound.³⁷

4534. In processes such as described in the preceding paragraph in which iodine or an iodine compound is used, the iodine compounds employed are such as are decomposed but slightly, if at all, at the reaction temperature (e.g., the alkali or alkaline earth iodides) and with these is used a substance which will cause dissociation of the iodine compounds, such as iron alum, ferric chloride, or copper sulphate. Tetrahydronaphthalene and benzene hydrocarbons may be produced from naphthalene, and ammonia and liquid hydrocarbons from coal-tar pitch.³⁸

²⁹ *Chem. Age* (London), 1927, **17**, 352; Brit. Pat. application, 275,664 (convention date, Aug. 7, 1926) by I. G.

^{29a} van Peski, Brit. Pat. 315,780, Jan. 18, 1928; *Brit. Chem. Abst.*, **1929**, 842B; cf. Brit. Pat. 315,193, *Brit. Chem. Abst.*, **1929**, 770B.

³⁰ Brit. Pat. application, 275,670 (convention date, Aug. 7, 1926) by the I. G.; *Chem. Age* (London), 1927, **17**, 352; cf. Brit. Pat. 295,587, July 9, 1927.

³¹ Brit. Pat. application 276,001 (convention date, Aug. 11, 1926) by I.G.

³² *Chem. Age* (London), 1927, **17**, 373.

³³ Brit. Pats (a) is 247,584 (convention date, Feb. 14, 1925), (b) is 247,585 (convention date, Feb. 16, 1925), (c) is 272,831 (Feb. 11, 1926), (d) is 272,832 Feb. 11, 1926), to I. G. Farbenind., A.-G.; *Brit. Chem. Abst.*, 1927, 595B.

³⁴ Brit. Pat. application 279,410 (addition to 277,974), convention date, Oct. 20, 1926, by Spilker, *et al.*

³⁵ *Chem. Age* (London), 1928, **17**, 579.

³⁶ Brit. Pat. applications 277,974, convention date, Sept. 23, 1926, and 279,055.

³⁷ *Chem. Age* (London), 1927, **17**, 496 and 557.

³⁸ *Chem. Abst.*, 1928, **22**, 2835; Spilker, Zerbe and Ges. f. Teerverwertung, Brit. Pat. 279,055, Oct. 18, 1926.

4534A. Pretreatment of Catalysts. It is said that catalysts for the destructive hydrogenation of coal, tars and mineral oils are improved by preheating with a non-reducing gas. Thus: molybdic acid is heated with carbon dioxide at 400° C., tungstic acid with nitric oxide at 350° C., a mixture of molybdic acid and chromium oxide with sulphur dioxide at 420° C.; a mixture of molybdic acid and silver oxide with nitrogen at 400° C., cobalt oxide with carbon dioxide at 350° C., cobalt oxide with carbon dioxide at 350° C., a mixture of molybdic and chromic acids with carbon dioxide at 400° C. and molybdenum wire wool with oxides of nitrogen.^{38a}

4534B. The catalytic material known as "Luxmasse," obtained as a by-product in the purification of bauxite and consisting mainly of alkaline ferric oxide, is increased in catalytic activity by mechanical, physical or chemical treatment (or a combination of these), as by repeated extraction with hot water and drying, or by dissolving in nitric acid and precipitating with ammonia, and is thus claimed to become more efficient in the hydrogenation of brown coal. It is stated that the catalytic activity of the material increases after its use in hydrogenation.^{38a}

4534C. According to Taylor^{38a} metallic hydrogenation catalysts are of little use for coal because of the presence of sulphide poisons. Oxide catalysts are better, such as potassium carbonate, zinc oxide, oxides of tungsten, chromium, etc. Oxides of thorium, aluminum, selenium, titanium and zirconium are good hydration-dehydration catalysts. Chromic oxide lies between the two groups. The presence of small quantities of alkali has a great effect, as in methanol synthesis. Metals of the platinum series and oxides and salts which may exist in two or more states of oxidation are important.

TWO-STAGE PROCESSES

4535. Two French processes³⁹ operate in two stages: (a) To carry the reaction out in this manner, the material is hydrogenated in the first and decomposed into separate fractions in the second. By heating a mixture of powdered bituminous coal and tar oils, in the proportion 2 : 1, directly at 440°–475° in the presence of hydrogen at 100 atmospheres pressure, no liquid product is obtained, but by heating first to 420° within twenty-four hours, and then at 440° for two hours, a 56.9 per cent yield of oil boiling to 330° is obtained. The amount of hydrogen taken up increases with the pressure, while the amount of decomposition varies inversely with the pressure. The yield and quality of the low-boiling fractions of the oil are better the greater the hydrogen absorption during the first stage. When a mixture of equal parts of coal and coal-tar residues is heated in the autoclave at 210° it becomes liquid, free carbon and ash settling out, but the yield of oil of low boiling-point is small. If, however, this product is again hydrogenated after the addition of 5 per cent of alkaline iron oxide a good yield of oil boiling to 230° is obtained. (b) The starting materials are pumped under pressure into the reaction chamber, which is provided with stirrers. The liquid reaction product can be discharged through a tube which dips below its surface, into a container fitted with a valve. The separation of the solid, liquid, and gaseous products is carried out under normal pressure.⁴⁰

4536. By a special modification of the catalytic procedure, motor fuel with anti-knock qualities, lubricating oils, etc., may be produced from carbonaceous material (coal, wood, bone tar, mineral oil residues, bitumen, resins, etc.) by interaction at high temperatures and pressures with water vapor or with gases containing hydrogen and oxides of carbon, in the presence of catalysts capable of forming methyl alcohol by the catalytic hydrogenation of oxides of carbon (vanadic acid, manganese, uranium, zinc, and titanous oxides, etc.). The initial material may be submitted to a preliminary hydrogenation, and it is preferable to allow only gases or finely divided material to come into contact with the catalyst, in a separate chamber.⁴¹

4537. (a) Coal or similar carbonaceous material is treated with hydrogen under pressures

^{38a} Brit. Pat. 311,251, Dec. 5, 1927 to Johnson (from I. G.); *Chem. Age* (London), 1929, 20, 593; I. G. Farbenind. A.-G., Ger. Pat. 489,279, July 31, 1927, Pier and Simon, inventors; *Chem. Abst.*, 1930, 2274.

^{39a} N.-V. de Bataafsche Petroleum Maatschappij, Brit. Pat. 314,859, July 3, 1928; *Chem. Abst.*, 1930, 1493.

^{39b} *Proc. 2nd Intern. Conference Bituminous Coal*, 1928, 1, 190–9; *Chem. Abst.*, 1930, 1200.

⁴⁰ French Pats. 606,189 and 606,191, to Soc. internat. des Combustibles liquides.

⁴¹ *Brit. Chem. Abst.*, 1927, 435B.

⁴² Brit. Pat. 257,256, Aug. 10, 1926; *Brit. Chem. Abst.*, 1926, 221B.

of at least 50 atmospheres and at high temperatures (e.g., under 200 atmospheres at 450°) with or without the aid of contact masses, and the tar-like products so obtained are further treated with hydrogen in the presence of catalysts under similar conditions of temperature and pressure. Seventy per cent or more of the carbon contained in the solid fuels is thereby converted into valuable hydrocarbons. (b) The tar vapors are subjected to the second stage of the treatment without condensing them intermediately.⁴²

4538. Pretreatment in presence of a cracking catalyst, followed by passage of the products over hydrogenation catalysts has been proposed.⁴³ High yields of low-boiling hydrocarbons are obtained from coal, tars, etc., by consecutive catalytic cracking and hydrogenation in the solid, liquid, or vapor phase. The cracking catalyst is stated to consist of elements of groups 3 and 4 of the periodic system, copper-iron mixtures or compounds, active charcoal or silica, and other substances. The hydrogenating catalysts are cobalt, molybdenum, tungsten, and their compounds. The process consists in treatment with hydrogen and the catalyst under pressure at 300°–700°, followed by the use of a different catalyst under similar conditions; it may be carried out with a large excess of hydrogen, so that the product has only a low partial pressure.⁴⁴

4539. The residues from berginization heated to a cracking temperature produce benzine and permanent gases.⁴⁵

4540. Multi-stage Hydrogenation of Coal Suspensions, Tars, Oils, etc. In the first stage hydrogenation is effected in the liquid phase under high pressure and, in the last, the products are heated in the vapor phase at low pressure. American crudes yield 75 per cent of hydrocarbons boiling below 200° C.⁴⁶

4541. The high-boiling products of the hydrogenation of coal at elevated temperatures and under high pressures are reintroduced into the pressure apparatus, the carbonaceous material being thereby further transformed into liquid and soluble products.⁴⁷

4542. During the destructive hydrogenation of coal, tar or mineral oils, effected in several stages, those constituents which are not affected by the first treatment are separated and then treated at a higher temperature.⁴⁸ Further stages and still higher temperatures may be employed, and in the final stage the material is employed in the form of vapor. Other chemical or physical treatment may be employed between the separate stages, and catalysts, particularly those of the sixth group, may be employed. Crude oil is thus hydrogenated to yield benzine, and coal likewise is hydrogenated to produce benzine and various oils.⁴⁸

4543. A process for the hydrogenation of carbonaceous material by heating with hydrogen under pressure consists of two stages, the first stage taking place at temperatures at which the principal reaction is hydrogenation, and the second at higher temperatures to split off hydrocarbons. Coal is heated to 470° in an autoclave with hydrogen at 100 atmospheres pressure for an hour and then at 290° for half an hour. Finally it is heated to 470° for another hour.⁴⁹

4544. Tars and oils may be subjected to destructive hydrogenation at elevated temperatures and pressures by passing the material, together with hydrogen, or gases supplying hydrogen, through more than two reaction vessels in series, so arranged that no appreciable cooling occurs between the separate reaction vessels. The material and the hydrogen may be preheated before entering the first reaction vessel, and the desired temperatures in the system maintained by suitably lagging the reaction vessels and connecting pipes, the reaction being exothermic.⁵⁰

⁴² Brit. Pat. 249,156 (a) and 274,404 (b), Mar. 13, 1926; cf. Brit. Pats. 247,582, -3 and -4; *Brit. Chem. Abst.*, 1927, 741B.

⁴³ I. G. Brit. Pat. application 273,712 (convention date, June 29, 1926).

⁴⁴ Cf. French Pats. 634,822, 634,820, May 21, 1927, to the I. G. Farbenind. A.-G.; *Chem. Abst.*, 1928, **22**, 3979.

⁴⁵ *Chem. Age*, 1928, **18**, 516; Brit. Pat. application, 288,148 (convention date, Mar. 31, 1927), by the I. G.

⁴⁶ *Chem. Age* (London), 1928, **19**, 466; Brit. Pat. application 296,431 (convention date, Sept. 1, 1927), by the I. G.

⁴⁷ Soc. Internat. des Combustibles Liquides, French Pat. 630,324, March 5, 1927; *Brit. Chem. Abst.*, 1930, 132B.

⁴⁸ I. G. Farbenind. A.-G., Brit. Pat. 320,473; *Chem. Age* (London), 1929, 575. See also French Pat. 663,539, Nov. 5, 1928, to same patentees; *Chem. Abst.*, 1930, 713.

⁴⁹ Ger. Pat. 490,636, Dec. 1, 1922, to Deutsche Bergin-A.-G. für Kohle- und Erdölchemie; *Chem. Abst.*, 1930, 2273.

⁵⁰ I. G. Farbenind. A.-G., Brit. Pat. 301,059, Sept. 3, 1928; *Brit. Chem. Abst.*, 1930, 449B.

4545. Destructive hydrogenation of carbonaceous materials in successive stages is effected with such regulation of pressure, temperature, hydrogen concentration and catalysts present that in the first stage the formation of gaseous and low boiling-point hydrocarbons is restricted, while in the final stages formation of the desired products is favored.⁵¹ Gaseous products at high temperature are removed in each stage. Suitable catalysts for the first stage are molybdenum or its compounds with or without iodine or its compounds: and iodine or its compounds may be used in the later stages.

4546. For the production of light hydrocarbons, low-temperature tars, lignites, or coals are heated with hydrogen under high pressures in the presence of dehydrating catalysts (cf. Brit. Pats. 263,082 and 276,007, *Brit. Chem. Abst.*, **1927**, 696B) and hydrogenating catalysts such as reduced iron, nickel, or cobalt, or unstable compounds, e.g., suboxides, sulphides, or nitrides, of tungsten, vanadium, molybdenum, uranium, iron, manganese, etc. The mixture may be heated successively at different temperatures, each corresponding with the optimum conditions for the action of one of the catalysts.⁵²

4547. Coal is heated with hydrogen under pressure, preferably with catalysts, to an appropriate reaction temperature when the heating is immediately stopped and the gaseous products are discharged. The products of high boiling point are heated with hydrogen under pressure and in the presence of catalysts to produce lower boiling products.⁵³

4548. According to British Patent 325,862, the destructive hydrogenation of coal and tars is carried out in stages and the carbonaceous substances of high molecular weight, which would otherwise choke the catalysts used in the later stages, are removed, for example, by conversion into products of lower molecular weight in the earlier stages of the process, or by condensation or adsorption before the material enters the second or later stages.⁵⁴

4549. Viscous oils and oils of low boiling point are obtained from liquid carbonaceous materials, such as brown coal tar, by first treating under "mild temperature conditions" (suitably at about 400°) with hydrogen under pressure, so that the paraffins are not destroyed, separating fractions suitable for making viscous oils and then cracking or destructively hydrogenating the residues to obtain oils of low boiling point. A catalyst containing molybdenum and zinc and pressure of 200 atmospheres may be used in the first stage.⁵⁵

4550. In effecting destructive hydrogenation of carbonaceous materials with aid of solvents, the extracts obtained are first treated in one or more stages without hydrogen and the products thus obtained are then treated with hydrogen or at higher temperatures. Hydrogenating catalysts such as finely distributed metals, metal oxides or acid anhydrides may be used in the preliminary stages, and "splitting" catalysts such as metal halides are used in the final stages.⁵⁶

⁵¹ Bataafsche Petroleum Maatschappij, Brit. Pat. 309,849, April 16, 1928; *Chem. Abst.*, **1930**, 713. See also French Pat. 671,974, March 23, 1929; *Chem. Abst.*, **1930**, 2275.

⁵² Florentin and Kling, Brit. Pat. 302,354, Nov. 30, 1928; *Brit. Chem. Abst.*, **1929**, 968B.

⁵³ De Bataafsche Petroleum Maatschappij, French Pat. 674,107, April 26, 1929; *Chem. Abst.*, **1930**, 2581.

⁵⁴ I. G. Farbenind. A.-G., Sept. 28, 1928; *Brit. Chem. Abst.*, **1930**, 449B.

⁵⁵ I. G. Farbenind. A.-G., Brit. Pat. 313,879, June 18, 1928; *Chem. Abst.*, **1930**, 1204.

⁵⁶ Pott and Broche, Brit. Pat. 309,446, April 10, 1928, *Chem. Abst.*, **1930**, 713.

CHAPTER XLVI

HYDROGENATION OF COAL AND RELATED HYDROCARBONS

III

HYDROGENOLYSIS PLANT AND INDUSTRIAL PROCESS

4600. A laboratory method for hydrogenating coal having been discovered, before it could be exploited commercially the following technical problems called for solution:

1. The prevention of local heating.
2. Temperature regulation.

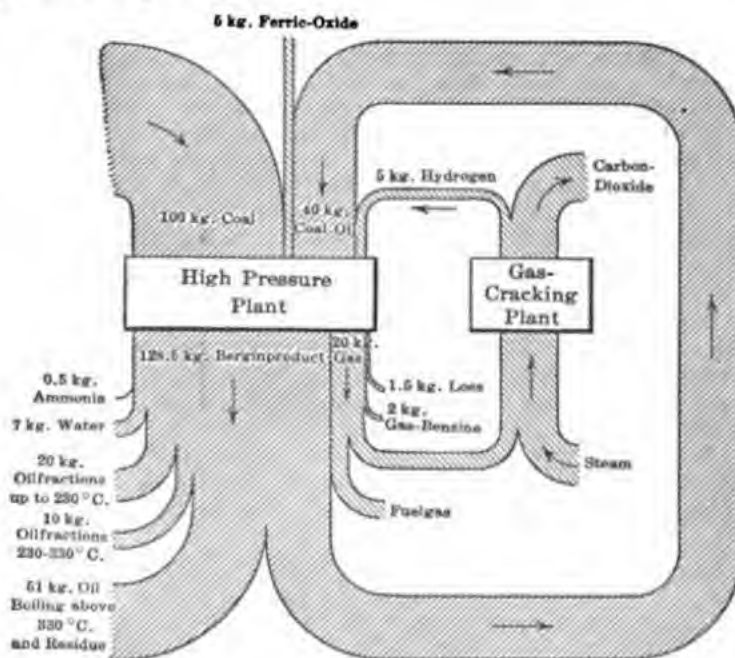


FIG. 97.—DIAGRAM ILLUSTRATING CONTINUOUS OPERATION OF BERGIN PLANT.

3. Conversion from a batch to a continuous process.
4. Heating without undue pressure on the walls of the reaction chamber.
5. The discovery of an economical source of hydrogen.

4601. Bergius¹ devised improvements in plant which consisted in (1) a stirring device, (2) circulation of the gaseous atmosphere. The circulation permits

¹ U. S. Pat. 1,391,664, Sept. 27, 1921 (application filed Apr. 18, 1916).

of the volatile products being removed from the reaction vessel and condensed. By the same means heat exchange and temperature regulation were facilitated, while local variations were prevented by agitation of the mass. Even to-day Bergius admits that temperature regulation is one of the most important factors in the successful technique.² The hydrogenation has to compete against carbonization. At 600° C. the latter process gains the upper hand.

4602. Method and Apparatus for Continuous Treatment of Coal or Hydrocarbons by Hydrogenation. The material to be distilled or hydrogenated under pressure is led into one end of a heated cylinder to the rotating axis of which a number of discs are attached. These discs divide the cylinder into compartments forming segments of the cylinder. The material under treatment passes by small openings at the edges of the discs from one chamber to another, and away by an exit at the far end of the cylinder. On leaving the cylinder the distilled material passes through a pipe which is cooled by water. This cooling renders it viscous so that it only flows slowly through a valve giving access to a chamber at ordinary pressure, thus enabling the high pressure within the chamber to be readily maintained. The pipe which conveys away the volatile matter is similarly cooled for like purposes.³

4603. In another step in the heat regulation ⁴ the hydrogen is preheated and circulated around the reaction chamber, but not in contact with the outer shell. It passes through an electric heater from the jacket into the reaction chamber.⁵

4604. In the same order of ideas we find ⁶ that in processes, such as the hydrogenation of oil or coal or the conversion of alcohols, e.g., methyl or ethyl alcohol into higher alcohols by the action of carbon monoxide or water-gas, the heat may be supplied wholly or partially by a preheated non-metallic gas which is not decomposed at the temperature of the reaction, but which is not necessarily inert. The gas is brought into direct contact with the materials and is preferably used in large amounts to avoid local overheating. The preheating is effected by means separate from the reaction vessel, and the preheater is protected from access of reaction products. The reacting materials may themselves be preheated, but not up to the temperature of the reaction.⁷

4605. Owing to the great experience in high-pressure technique acquired especially in ammonia synthesis, the art has reached a high degree of perfection. Working at high pressure, in itself, is no longer a disadvantage. On the contrary, when large volumes of gas are to be handled and especially when efficient heat exchanges are desired, high pressure is almost essential.

4606. Yet, at the temperature of berginization, the metal wall of the reaction chamber is much weakened. Therefore the walls would yield, if exposed to the full pressure while being directly heated. To obviate this, and at the same time to provide an effective means of heat regulation, the reaction chamber is jacketed. In this jacket is circulated, under pressure slightly less than that in the reaction

² Pittsburgh Conference on Bituminous Coal, 1926.

³ Ger. Pat. 389,946, Nov. 4, 1920, to Erdöl & Kohle-Verwertung A.-G. and Debo. See Can. Pat. 258,201, May 15, 1925, to Internat. Bergin-Comp., assignees of Debo.

⁴ Brit. Pat. application 287,855, Mar. 26, 1927, to the I. G.

⁵ *Chem. Age* (London), 1928, 18, 516; cf. French Pat. 638,325, July 27, 1927, to the same patentee; *Chem. Abst.*, 1929, 23, 265; also Can. Pat. 283,921, Oct. 9, 1928, to Pier, Wildhagen and Schunck (assigned to the I. G.).

⁶ Brit. Pat. 275,248, July 28, 1927, to the I. G.

⁷ *Brit. Chem. Abst.*, 1929, 78B.

vessel, a hot, indifferent gas, such as nitrogen or carbon dioxide. This gas is heated in an independent furnace and by suitable heat exchange devices, serves to maintain the desired temperature.

4607. It is said that, in the large scale plants, the temperature is maintained constant within 5°C . during weeks of continuous operation. At Mannheim and

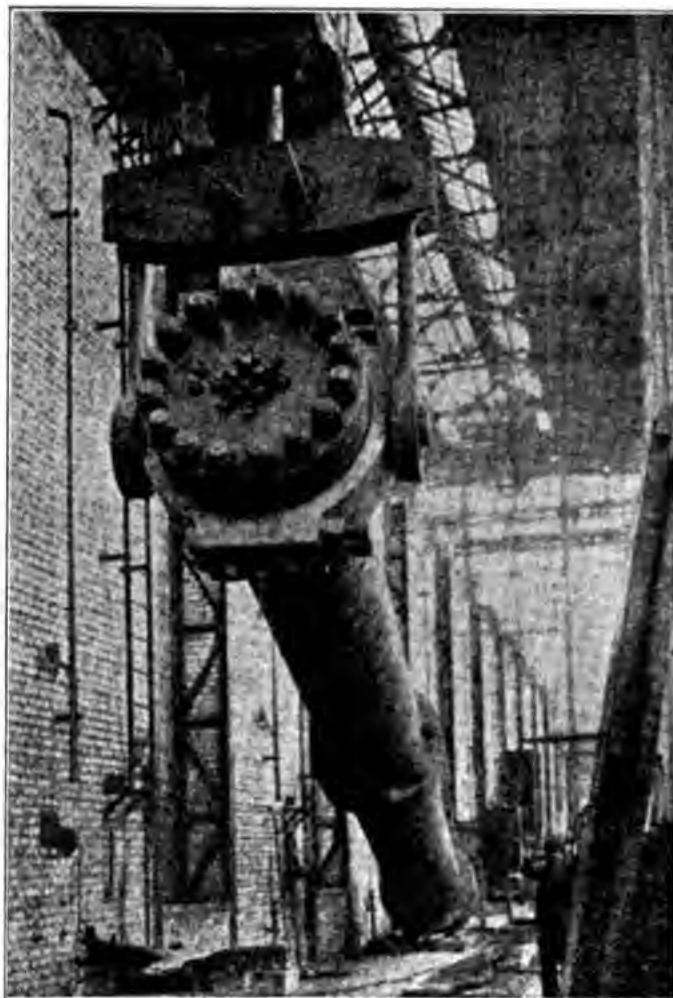


FIG. 98.—HYDROGENATION REACTOR NEARLY ASSEMBLED.^{7a}

at the British Fuel Research Station three reaction vessels are used in series: the temperature in the first is about $460^{\circ}\text{--}480^{\circ}\text{C}$., in the other two 490°C . The temperature in the last is important and depends on the special characters of the raw material.⁸ Each of these vessels is about 8 meters long and 80 cm. in internal diameter, with a working capacity of 20 tons in twenty-four hours.

^{7a} Wilke, *Brennstoff und Wärmewirtschaft*, 1929, Vol. 22. Wilhelm Knapp, publisher, Halle.

⁸ Lander, *Chem. Age* (London), 1929, **20**, 120.

4608. The use of this pressure-relieving and temperature maintaining jacket is claimed in Brit. Pat. 192,849, Nov. 30, 1921, to Bergius and Löffler. In preparing light hydrocarbons by heating heavy hydrocarbons or mineral oils (which may be mixed with coal), under pressure as described in Brit. Pat. 25,510, 1913,⁹ or under pressure with hydrogen as described in Brit. Pats. 4574, 1914, and 18,232, 1914,¹⁰ the reaction chamber is heated by hot gases such as carbon dioxide or flue gases, circulating in a surrounding jacket under a pressure about equal to that in the reaction chamber. A slight difference of pressure indicated by a water column may be used to show if the walls of the reaction chamber sustain damage. The oil or mixture of oil and coal, prepared as described in Brit. Pat. 192,850 (to Bergius and Löffler) is fed from a tank through a heater and hydrogen from a receiver through a heater. Vapors from the reaction chamber pass to condensers; the residue is withdrawn through another pipe. The gas from the jacket is circulated through a heat transfer apparatus.¹¹

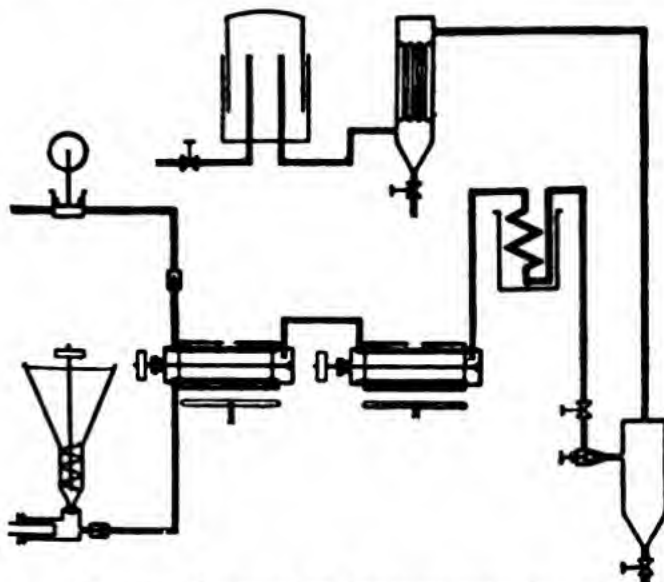


FIG. 99.—DIAGRAM OF BERGINIZATION PLANT.*

4609. Brit. Pat. 192,850, Nov. 30, 1921, to Bergius and Löffler, describes the same construction for the berginization of heavy hydrocarbon oils mixed with solid fuels, and prescribes heating the materials nearly to the reaction temperature before introducing them into the reaction chamber.¹²

4610. Reference is made to this patent in Brit. Pat. 282,814, to I. G. Farbenind. A.-G. (convention date, Aug. 14, 1925). In this the destructive hydrogenation of oils, tars, resins, etc., is described as taking place in a vessel of manganese bronze. The products before being cooled may be passed over a molybdenum catalyst.

4610A. In another process, at least a part of the heat necessary to bring the reaction chamber to the required temperature is furnished by admitting compressed hydrogen to the chamber at a temperature above the normal reaction temperature.^{12a}

4610B. Ulke describes a horizontally inclined rotatable retort provided with a double wall adapted to contain a temperature-regulating medium.^{12b}

* To Graefe and v. Walther, applies to mineral oils.

⁹ To Bergius, the original Brit. pat. for berginization of coal.

¹¹ *Chem. Abst.*, 1923, 17, 3247. U. S. Pat. 1,592,772, July 13, 1926, to Bergius describes the double-wall construction, with an inert gas circulating in the interspace at the same pressure as that prevailing in the reaction chamber.

(By courtesy of *Scientific American*.)

¹² *Chem. Abst.*, 1923, 17, 3247; Ger. Pat. 303,332, Apr. 1, 1915; *J.S.C.I.*, 1922, 41, 850A.

^{12a} Florentin and Kling, Brit. Pat. 308,712, March 27, 1928; *Chem. Abst.*, 1930, 489.

^{12b} U. S. Pat. 1,449,875, March 27, 1923.

4611. Fractional Hydrogenolysis.¹³ Hydrogenation, fraction by fraction, of liquid hydrocarbons produced by berginization or otherwise has been described. The starting materials, if liquid, are separated into fractions of narrow boiling-point range, each fraction being then subjected separately to destructive hydrogenation under pressure. If the initial material is solid, it is first converted wholly or partially, by some known process, into liquid products. Liquid starting materials may also be subjected to a preliminary hydrogenation, with or

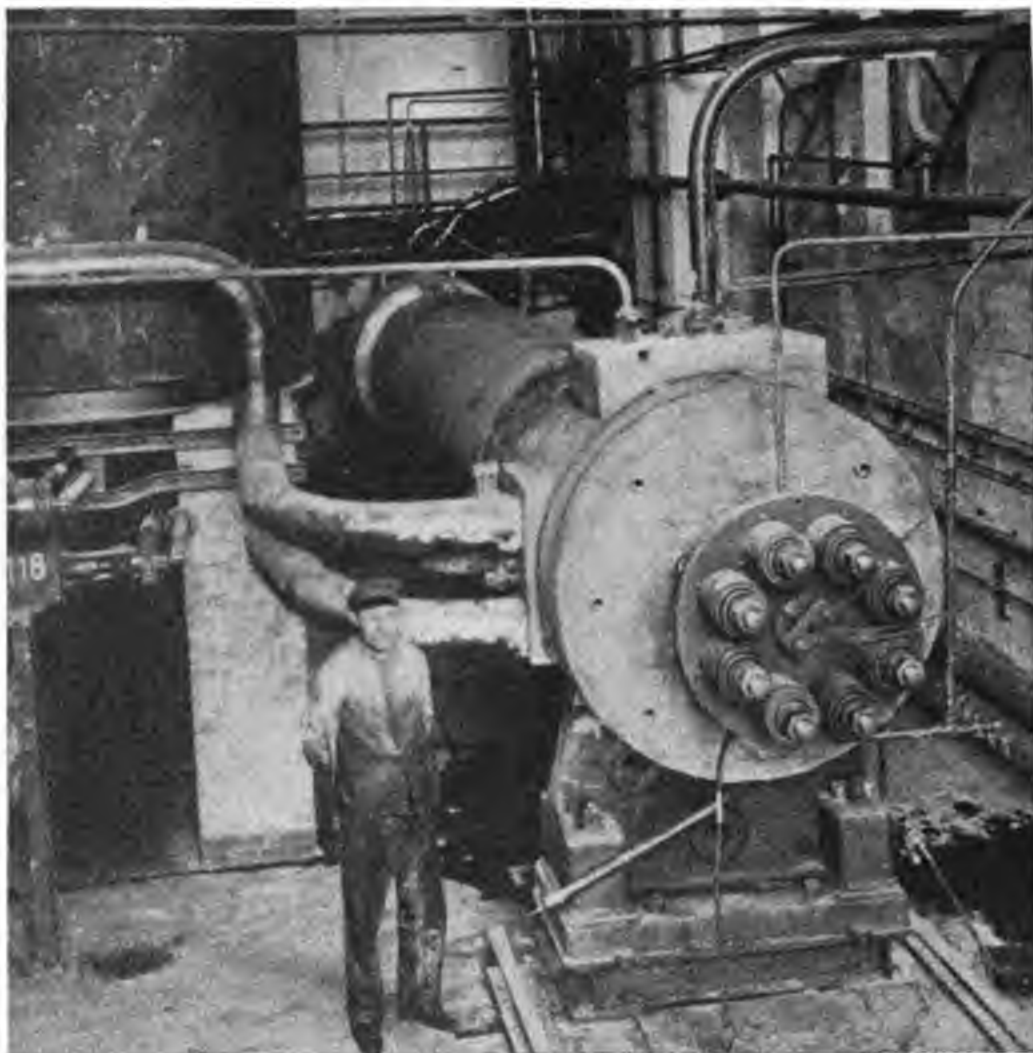


FIG. 100.—HIGH-PRESSURE HYDROGENATOR FORMING PART OF A COAL-LIQUEFACTION PLANT.

The hydrogenator is 3 feet in diameter and 24 feet in length and withstands pressures of more than 2000 lbs. per square inch. (Bergius, *Sci. Am.*, 1929, 322.)*

without the employment of pressure or catalysts, in order to modify their boiling ranges, before submitting them to the described process.¹⁴

4612. Pressure Regulation in the Hydrogenation of Coal. The hydrogenation is carried out at 450° under a pressure of 150–200 atmospheres in three chambers. The partially hydrogenated product from the first chamber passes into a separating vessel, from which

¹³ Brit. Pat. 273,337, June 27, 1927, to I. G. Farbenind. A.-G.

*Courtesy of *Scientific American*.

¹⁴ *Brit. Chem. Abst.*, 1928, 561B.

the volatile products are allowed to escape; the liquid, however, passes into the second chamber in which it is further hydrogenated. The process is repeated in the third chamber. The escaping volatile products are cooled and condensed.¹⁵

4612A. In the liquefaction of coal by heating it under pressure with hydrogen, the pressure is caused to alternate rapidly (suitably at the rate of 10 cycles per min.^{16a})

4612B. In effecting destructive hydrogenation of coals, tars and oils, the gases and vapors are maintained at a higher rate of flow in the reaction space by setting up a pulsating or oscillating movement of the gases. This is brought about by the action of a piston.^{16b}

4613. Charging the Reaction Vessel.¹⁶ An apparatus for charging solid materials into high-pressure reaction vessels comprises a piston which operates in a receptacle communicating by wide gates or valves with the reaction vessel or with the atmosphere. An air-lock device is provided with an outlet valve (to the main reaction vessel) having a large opening, while the other closure or inlet valve is formed as a piston which when depressed forces the material into the main chamber and at the same time displaces nearly all the high-pressure gas out of the air-lock chamber. The piston is not withdrawn until after the outlet valve is closed.¹⁷

4613A. Introducing Liquid or Semi-liquid Materials into High-pressure Vessels.^{17a} Material such as a mixture of oil and coal is pumped by two plunger pumps in series, and between them is an intermediate receiver comprising a cylinder with differential piston, to the smaller side of which the paste is admitted, while the larger side is subjected to the pressure of a gas, which may be the same as that in the high-pressure vessel to be charged.

4614. Construction: Materials.¹⁸ The reaction vessel and other parts of the apparatus which come into contact with the hot organic reacting materials in hydrogenation processes carried out under high pressures are made of, or coated with, materials, e.g., alloys containing one or more of the metals nickel, cobalt, molybdenum, tungsten, etc., or of the metalloids boron, arsenic, antimony, silicon, etc., which do not give rise to the formation of methane or to the deposition of carbon. Copper or its alloys may be used if the reacting materials are free from sulphur. Metals or alloys prepared by fusion *in vacuo* and free from impurities at the boundaries of the crystal grains are particularly suitable for the purpose.¹⁹

4614A. Absorption of hydrogen by the steel used in hydrogenolysis apparatus has been studied at the (British) National Physical Laboratory. A mild steel used at the Fuel Research Station and which had become brittle was found to contain 180 cc. of hydrogen per 100 g.²⁰

4614B. In the treatment of coal, tars or mineral oils with hydrogen under pressure, the presence of iron, nickel and copper (the latter only in the case of the presence of sulphur) is excluded from the heated part of the reaction chamber and parts of the apparatus in contact with products containing sulphur and hydrocarbons above 300°. Aluminum alloys high in aluminum, chromium, cobalt, molybdenum, tungsten, vanadium or manganese may be utilized, and if sulphur be absent silver or copper or their alloys may be used.^{20a}

¹⁵ *Brit. Chem. Abst.*, **1928**, 115B; French Pat. 618,674, July 8, 1926 (German date, Dec. 15, 1925), to Soc. Internat. des Combust. Liq.

^{16a} Kastner, *Brit. Pat.* 314,491, June 28, 1928; *Chem. Abst.*, **1930**, 1493.

^{16b} I. G. Farbenind. A.-G., *Brit. Pat.* 304,343, Oct. 17, 1927; *Chem. Abst.*, **1929**, 4802.

¹⁷ French Pat. 637,386, July 9, 1927, and *Brit. Pat.* 274,122, July 11, 1927, to I. G. Farbenind. A.-G.

^{17a} *Brit. Chem. Abst.*, **1928**, 802B.

¹⁸ Boyce, Tate and Imperial Chem. Industries, Ltd., *Brit. Pat.* 322,645, Dec. 7, 1928; *Brit. Chem. Abst.*, **1930**, 127B.

¹⁹ *Brit. Pat.* 275,662, Aug. 8, 1927, to I. G. Farbenind. A.-G.

²⁰ *Brit. Chem. Abst.*, **1928**, 738B.

^{20a} *Chem. Age* (London), 1928, 18, 607.

²¹ I. G. Farbenind. A.-G., French Pat. 34,590, Nov. 29, 1927; Addn. to 612,503; *Chem. Abst.*, **1930**, 1494.

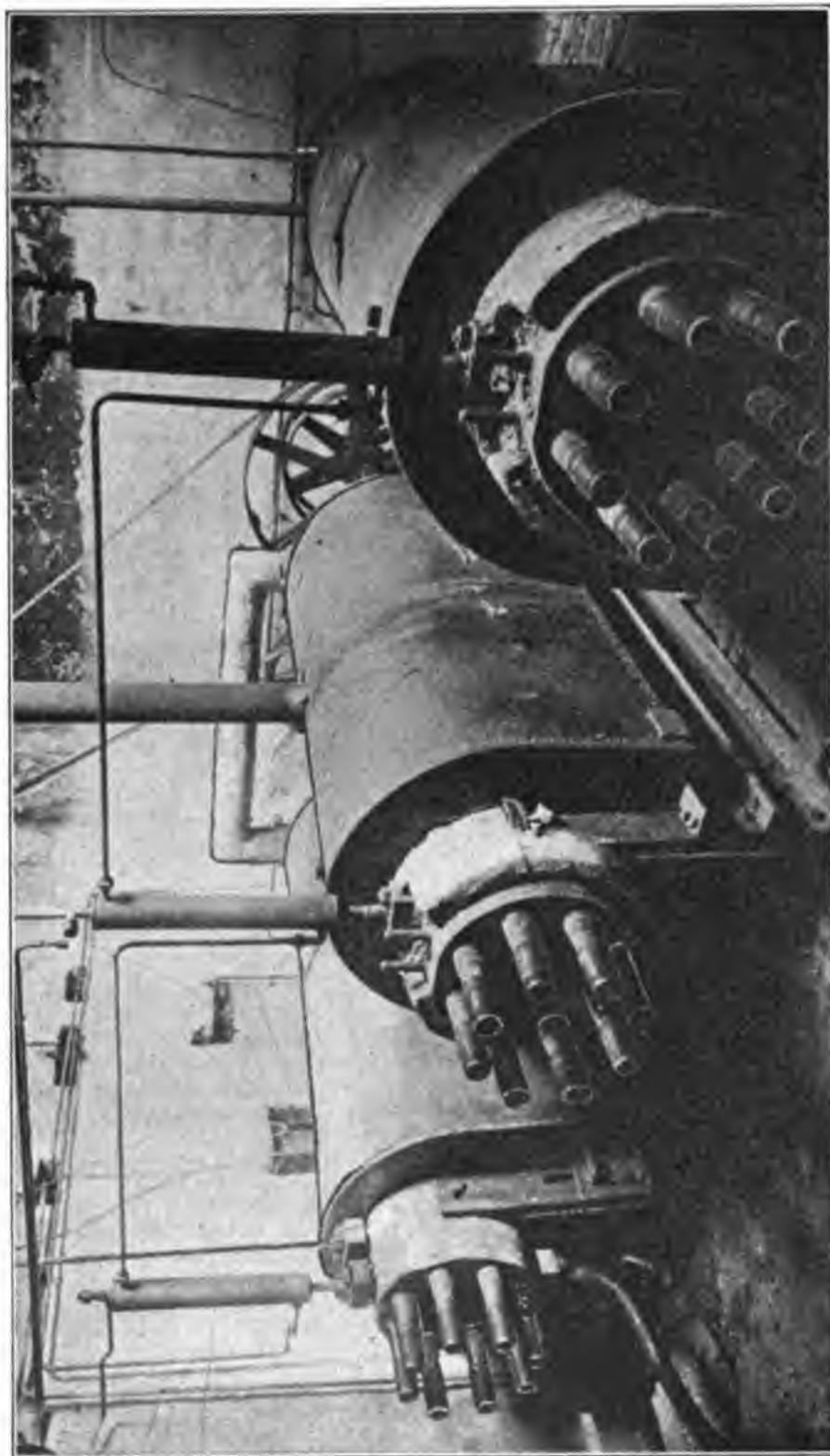


FIG. 101.—VIEW OF HYDROGENATION PLANT IN AN EXPERIMENTAL STATION AT MANNHEIM-RHEINAU, GERMANY, HAVING CAPACITY SUFFICIENT TO HYDROGENATE ONE TON OF COAL DAILY. (Bergius, *Sci. Am.*, 1929, 322.)*

4615. Construction Material Available in Absence of Carbon Monoxide. One advantage supposed to arise from the complete removal of carbon monoxide from the reacting gases is the greater choice of construction materials available.²¹ When the hydrogenating gases are substantially free from carbon monoxide or substances leading to the formation of carbon monoxide, the reaction chamber and such parts of the apparatus exposed to temperatures over 300° C. are constructed from materials free from uncombined iron and nickel, and also from copper and silver if sulphur is present. The apparatus is preferably constructed of aluminum, or of chromium, molybdenum, tungsten, vanadium, manganese. The alloys may contain a high percentage of nickel and should have a low carbon content (i.e., below 0.5 per cent). The steels V2A and WT₁, made by Krupp, containing respectively besides iron (1) 20 per cent chromium, 7 per cent nickel, 0.1–0.3 per cent carbon, and (2) 18 per cent chromium, 60 per cent nickel, 0.2 per cent carbon are suitable; also the chromium nickel alloy B made by Heraeus containing 24.2 per cent iron, 60.1 per cent nickel, 13.38 per cent chromium, and 0.02 per cent carbon. The alloys used should be freed from impurities in the boundaries of the grains by treatment with moist hydrogen.²²

4615A. For destructive hydrogenation of carbonaceous materials an apparatus ^{22a} is used the inner wall of which is preferably composed of an alloy steel highly resistant to chemical action and the outer wall of steel of high mechanical strength or impervious to hydrogen. Chromium-nickel (V2A), chromium-vanadium and chromium-tungsten steels are suitable.

4616. In the first plants only those parts which were exposed to high temperatures were made of the special materials resistant to carbon monoxide.²³ Later, it seems to have been found necessary to use the same, or equally resistant materials for the cooler parts.

4617. The walls of the reaction vessels may serve as electrical resistances, by which the necessary heat may be communicated. Thus, tar is passed slowly under hydrogen pressure through a long tube made of an iron-nickel-chromium alloy heated by an electric current to 420° C. The alloy contains 60–65 per cent nickel, 10–15 per cent chromium, and is low in carbon.²⁴

4617A. In another apparatus ^{24a} for the hydrogenation of coal, oil, or the like, the reaction vessel is so designed that the walls are protected, by an incoming stream of comparatively cool oil or coal-oil mixture, from the action of hydrogen at high temperatures. Thus, by means of a suitable baffle, the incoming stream, at say 200°, may be made to flow down in contact with the wall of the high-pressure vessel and thence up into the reaction space, which is maintained at the necessary high temperature by introducing the hydrogen at about 500°.

*Courtesy of *Scientific American*.

²¹ Brit. Pat. 282,384 (convention date, Dec. 20, 1926), to I. G. Farbenind. A.-G.

²² *Ill. Off. J.*, Feb. 15, 1928; *Univ. Oil Prod. Co. Bull.*, Mar. 10, 1928; Can. Pat. 283,916, Oct. 9, 1928, to Pier and Rumpf (assigned to the I. G.), differs but slightly in its specifications from the patent described in the preceding paragraph, although the apparatus may be used with gases containing carbon monoxide. Cf. *Chem. Abst.*, 1929, **23**, 691.

^{22a} I. G. Farbenind. A.-G., Brit. Pat. 309,057, Dec. 2, 1927; *Chem. Abst.*, 1930, 490.

²³ Cf., Brit. Pats. 247,217 and 249,155 to the I. G. to which 277,273 is an addition.

²⁴ Brit. Pat. 279,825 (convention date, Oct. 28, 1926) to I. G.

^{24a} Gordon and Imp. Chem. Ind., Ltd., Brit. Pat. 315,513, May 12, 1929; *Brit. Chem. Abst.*, 1929, 803B; *Chem. Abst.*, 1930, 1725.

PRETREATMENT OF MATERIAL

4618. In addition to the obvious step of grinding the coal, various other pre-treatments of the raw material have been used, some to facilitate the conversion, others to predetermine the nature of the products.

4619. Reduction of Ash by Flotation. In order to reduce the mineral content of coal intended for hydrogenation ²⁶ the pulverized fuel is treated with a hydrocarbon oil and an aqueous liquid. The bulk of the ash remains with the water.

4620. Gravity separation by use of a bath of suitable density is the method of coal cleaning adopted by Lessing.²⁶ But, as he calls for removal of fine coal before the treatment, his method will hardly be used to prepare coal for berginization. As separation of minerals by use of a fluid of intermediate density is a method of respectable antiquity, Lessing's invention must consist in some new apparatus or device for applying it. One modification leaves part of the bath solution with the coal to act as a catalyst in hydrogenation.

4620A. Prior to destructive hydrogenation, coal is treated to remove part of its content of fusain or durain, as by crushing and separating the fines, and hand picking. The caking properties of the coal may be modified by a preliminary hydrogenation, by preheating in the absence of air to 100°–350°, by heating in the presence of air, oxygen, steam, hydrocarbons or inert gases under pressure to 300°, by exposure to air or oxygen for long periods or by treating with various oxidizing reagents.^{26a}

4620B. A mixture of powdered coal with a liquid vehicle is conveyed over the greater part of the distance between a mixer and a converter in the form of a relatively thin suspension, and is passed into a settling vessel from which the thicker and thinner suspensions are drawn off, the former being supplied to the hydrogenation converter while the latter is returned to the mixer. If desired, the thin suspension may be passed through a heater on its way to the settling tank.^{26a}

4621. Preparation of Material for Berginization—Removal of Water.²⁷ Moist solid fuels, mixed with oil from previous batch, are centrifuged to remove water.²⁸

4622. Drying of Fuel before Berginization.²⁹ This is effected by heating moist fuels under pressure to 200° C. and removing the separated water, a procedure facilitated by stirring, centrifuging, action of an electric field, or addition of aniline or alkyl sulphonates.³⁰ These provisions for removal of water contrast with the process described in para. 4623.

4622A. Carbonaceous materials are subjected to a preliminary treatment by distilling off water in the presence of an organic solvent such as mineral and tar oils of high boiling point, naphthalene, anthracene, etc. The distillation may be effected at reduced pressure or in the presence of scavenging gases. High pressures may also be used, and the process may be effected in several stages at 300°–450° C.^{30a}

4623. Hydrogenolysis of Coals, Tar, etc. (specifically of brown coal tar) Prevention of Coking.³¹ By starting with wet material, or by adding water prior to berginization, coking is avoided. For example, brown-coal producer tar containing 40–50 per cent of water is pumped into a high-pressure reaction vessel in which it is vaporized or atomized with hydrogen, and then at 200 atmospheres and at 450–500° is passed over a catalyst containing molybdenum. The issuing vapors are condensed, and benzene and other petroleum hydrocarbons separated from the water.

²⁶ Brit. Pat. 296,536; French Pat. 639,681, Aug. 19, 1927; U. S. Pat. to Howard, 1,702,899, Feb. 19, 1929, assigned to Standard Oil Development Co.

^{26a} Brit. Pat. 282,874, Sept. 27, 1926.

^{26b} Lander, Sinnatt and King, Brit. Pat., 306,564, Sept. 17, 1927; *Chem. Abst.*, 1929, 5032.

^{26c} Tate, Stephenson and Imperial Chem. Industries, Ltd., Brit. Pat. 322, 917, Dec. 31, 1928; *Brit. Chem. Abst.*, 1930, 229B.

²⁷ Brit. Pat. 262,099, Nov. 26, 1925, to I. G. Farbenind. A.-G.

²⁸ *Chem. Age* (London), 1927, 16, 397, 144.

²⁹ Brit. Pat. 274,858, July 21, 1926, to the I. G.

³⁰ *Chem. Abst.*, 1928, 22, 2259.

^{30a} I. G. Farbenind. A.-G., Brit. Pat. 320,918, Appln. date, May 21, 1928; *Chem. Age* (London), 1929, 628.

³¹ Brit. Pat. 257,910 (convention date, Sept. 2, 1925) to I. G. Farbenind. A.-G.

4624. Pretreatment of Coal, etc. Pott and Broche³² subject coal to an extraction process before hydrogenation. Prior to the treatment of coals and like solid carbonaceous materials in suspension in oil with hydrogen under pressure to obtain benzines, the solid materials are first disintegrated by treatment with solvents, e.g., tetralin, under increased temperatures and pressures corresponding to the tension of the solvent. The disintegration treatment is conducted in stages so that the temperature used in each step lies close to the decomposition temperature of the residual portion of the material. Five hundred grams powdered gas carbon are treated with 1000 cc. tetralin in four extractions at 320, 350, 380, 400° C. Over 70 per cent of the carbon passes into solution and after separation of ash and removal of solvent a pitch-like glittering mass is obtained which melts when heated and is suitable for conversion into benzines, etc. Examples are given of the treatment of caking coals and coal extracts.³³

4625. The process described in the preceding paragraph has much in common with that set out below.³⁴ Oils and other organic products are obtained from coal and other solid carbonaceous materials by treatment at pressures of at least 75 atmospheres and at temperatures below the coking temperatures of the extracting agent, with such hydrocarbons or their derivatives as are liquid under the reactive conditions, contain substantially no components boiling below 100° C., and boil mainly between 100° and 300° C. Catalysts and gases substantially free from hydrogen may be present. The treatment may be conducted in stages at different pressures, lower pressures than 75 atmospheres being used initially if desired. Pressures up to 1000 atmospheres are specified; temperatures of 300°–400° C. are preferable. The oils may be worked up into Diesel oils, lubricating oils, insulating oils, and the like, or be used for the treatment of fresh coal; or they or the solid residue may be treated with hydrogen in presence or absence of catalysts and pressure to produce middle oils, benzine, and the like. Extracting agents specified are xylene, cresol, hydrogenated naphthalenes, aniline, alkaline substances decomposing coal, oils boiling above 180° C. obtained by the process, oils resulting from the distillation of low-temperature carbonized coal, lignite, or mineral oils, or from the destructive hydrogenation of coal, tars, mineral oils, etc., or from the catalytic hydrogenation of oxides of carbon under pressure.³⁵

4626. Anti-knock Fuel by Hydrogenolysis.³⁶ The pretreatment of highly bituminous coal with a solvent (e.g., gasoline) to remove bitumen, causes the product obtained from the coal by subsequent treatment with hydrogen to possess anti-knock properties.

4627. The addition of lignite or peat to the raw materials (other than lignite or peat) for berginization leads to an increased yield of liquid products and diminishes the tendency to coke formation. The raw mixtures so formed flow under high pressure like viscous fluids.³⁷

4628. Preheating Raw Material. Liquid hydrocarbons or carbonaceous pastes which are to be subjected to destructive hydrogenation or other process involving high temperatures are preheated in vessels or tubes the walls of which act as electrical resistances and are traversed by a heating current. Iron pipes may be used for the purpose up to about 400°, but if higher temperatures are used the pipes should be constructed of aluminum or chromium-nickel steel in order to prevent carbon deposition or methane formation.³⁸

4628A. Solid carbonaceous materials, such as coal, peat or wood, are heated under pressure (which may be as high as 1000 atmospheres) at temperatures below the coking point of the initial materials (suitably 200°–450°), previous to cracking or destructive hydrogenation.^{39a} Water, alkaline substances such as alkaline sulphides and other inert or catalytic substances such as iodine or molten or liquid metals such as lead, tin, bismuth, mercury or alloys of low melting point may be added. An example is given of such a preliminary treatment of brown coal, followed by catalytic hydrogenation of liquid products thus obtained.

4629. Desulphurization.³⁹ Coal pastes, tars, oils, etc., containing sulphur, are treated

³² Brit. Pat. 293,808 (convention date, July 12, 1927).

³³ *Ill. Off. J.*, Sept. 15, 1928; *Univ. Oil Prod. Co. Bull.*, Oct. 3, 1928.

³⁴ Brit. Pat. 283,545, Dec. 21, 1927, to I. G. Farbenind. A.-G.

³⁵ *Ill. Off. J.*, Mar. 7, 1928; *Univ. Oil Prod. Co. Bull.*, Apr. 7, 1928.

³⁶ Brit. Pat. 281,247, Nov. 26, 1926, to I. G. Farbenind. A.-G.

³⁷ Brit. Pat. 256,964, Aug. 10, 1926.

³⁸ *Brit. Chem. Abst.*, 1928, 738B; Brit. Pat. 279,825, Oct. 13, 1927, to I. G. Farbenind. A.-G.

^{39a} I. G. Farbenind. A.-G., Brit. Pat. 308,633, Dec. 21, 1927; *Chem. Abst.*, 1930, 490.

³⁹ Brit. Pat. application 296,429 by the I. G. Farbenind. A.-G., convention date, Sept. 1, 1927.

with hydrogen in presence of a catalyst (e.g., molybdenum) in the liquid phase, to eliminate sulphur and asphalt.

RELEASE OF PRESSURE

4630. Utilization of the Energy of Gas Compression.⁴⁰ After the usual berginization series of operations the residual permanent gases, still under pressure, are expanded to atmospheric pressure in an engine.⁴¹

4630A. After preliminary separation of liquids from associated gas and vapor (suitably in an apparatus as described in British Patent 310,985), condensable vapors may be removed by cooling or scrubbing, and the gas may be expanded in an engine and the liquid utilized to drive a Pelton wheel.^{41a}

4631. According to Lander⁴² the vapors leaving the last reaction vessel are cooled and the pressure released in two stages: first, to 60 atmospheres at which pressure they are scrubbed with oil to remove gasoline and then to atmospheric pressure at which the final crude product is collected.

RECOVERY OF PRODUCTS

4632. Berginization, Recovery of Products. Water having been removed from the crude product of the berginization of coal, the bituminous material is mixed with aliphatic hydrocarbons, such as gas-oil. First the unaltered coal settles out and, afterwards, the asphalt. For example, all substances, including water, distilling up to 280° C. having been removed, the residue is mixed with one-fifth of its volume of raw petroleum. After one hour the liquid is decanted, bearing asphalt and other solids. After three to five hours it is again decanted from soft asphalt. The oil is then fractionally distilled to obtain light lubricants and gas-oils.⁴³

4633. Purification of the Liquid Complex Hydrocarbon Products. The crude liquid hydrogenation products are treated with one of the lower aliphatic alcohols (e.g., crude synthetic methyl alcohol obtained by the catalytic hydrogenation of carbon monoxide). The treatment is preferably carried out by a counter-current method, the solid paraffins having first been separated from the crude oils at -10°. The impurities dissolve in the alcohol and highly refined products are obtained, suitable for use as lubricating oils, etc.⁴⁴

4633A. In the separation by solvents of the oils from the solid residues obtained in destructive hydrogenation, the solvent and material treated are introduced continuously to the extractor, and the oil-free residue and the extract are continuously removed. In a countercurrent process, 200 kg. per hour of hot sludge from a high-pressure vessel of the destructive-hydrogenation plant is discharged through a valve into a heat-exchanger, and passes by a pipe and a distributor to an extractor; it is agitated by stirrers and falls by gravity to a discharging worm; 300-400 liters per hour of benzol is forced in at the lower end, and rises to a settling chamber fitted or not with a filter. The extract flows by a pipe to the exchanger maintained at 140-160° C. so that the benzol distills over to a condenser, and flows through a collector, a meter, an inspection chamber, and a pump to the extractor. The extractor is kept at about 45-55° C. The product may be destructively hydrogenated, or used to triturate coal to be so hydrogenated.^{44a}

⁴⁰ Brit. Pat. 280,734, Jan. 10, 1927, to the Internat. Bergin Co. of Holland and to Debo.

⁴¹ *Chem. Age* (London), 1928, 17, 577.

^{41a} Harrison and Imperial Chem. Industries, Ltd., Brit. Pat. 311,193, Dec. 31, 1927; *Chem. Abst.*, 1930, 670.

⁴² *Chem. Age* (London), 1929, 20, 120.

⁴³ Brit. Pat. 262,738, Dec. 11, 1925, to Deutsche Bergin. A.-G. Kohle- u. Erdolchemie; *Chem. Age* (London), Feb. 19, 1927, 189; U. S. Pat. 1,709,957, Apr. 23, 1929, to Schoenemann.

⁴⁴ Brit. Pat. 257,270, Aug. 18, 1926, to the I. G.; *Brit. Chem. Abst.*, 1928, 359B.

^{44a} Brit. Pat. 312,657, Feb. 20, 1928, to the I. G.

4633B. Oils are separated from mixtures with solid substance, such as sludge obtained by the destructive hydrogenation of brown coal, by adding a wetting agent and a solvent for the oil and centrifuging.^{44a}

4633C. Oils contained in the residues from the hydrogenation under pressure of coal, tars and mineral oils, are recovered by continuous circulation of the residues and a solvent in opposite directions. The hydrogenation products having a high content of aromatic compounds may be used as solvents and are recovered.^{44a}

4633D. Extraction of hydrocarbons from coal, tars, mineral oils, etc., with liquid organic solvents under pressure is effected in the presence of organic wetting or emulsifying agents, with or without addition of hydrogen or other suitable gas or use of alkalis, magnesium oxide or zinc oxide.^{44a}

4633E. In order to separate the oils from solid residues of varieties of coal, tars, and mineral oils under pressure, the residues are mixed with solvents and the mixture filtered in an apparatus to and from which the solvent, the mixture, the extracted products, and the extracted residues are continuously supplied and removed. The solvents used are preferably oils of boiling range 150°–300°, derived from the destructive hydrogenation process itself. The residues from the filter may be subjected to a subsequent low-temperature carbonization.^{44a}

4633F. Liquid or readily liquefiable products are obtained from solid distillable carbonaceous materials such as coals, oil shales or other bituminous substances by destructive hydrogenation "under mild conditions" so that the formation of benzene is substantially avoided, followed by extraction with solvents. Brown coal may be treated at 450° under 200 atmospheres pressure with a counter-current of hydrogen.^{44f}

4634. The crude viscous distillate is treated with benzene or light petroleum and with a small quantity of a mineral acid, whereby the resinous matter is coagulated and may be separated by filtration. The remaining oils are then separated by fractional distillation or by chemical treatment.⁴⁵

4634A. Tars from the carbonization at low temperatures of coal, oils obtained from this or other tar, as well as oils from the hydrogenation under pressure of coal, tars or mineral oils are refined by treatment (preferably after a preliminary treatment with hydrochloric acid and elimination of the acid tar thus formed) by a mineral acid, such as sulphuric acid or hydrochloric acid, dissolved in alcohol or other organic solvent.^{45a}

4634B. Oils are recovered from the oil-bearing residues of the destructive hydrogenation of coal, tars or mineral oils or the residues from the extraction of coal under pressure by benzene. These residues are mixed with coal dust, sawdust or the like, and oils from the residues are obtained mixed with the oils from the powdered fuels and are suitable as a "pasting medium" for destructive hydrogenation. Coke ash or clinker may be added to promote, catalytically, the formation of low boiling-point hydrocarbons or to loosen the starting material.^{45a}

4635. Products of berginization are among those to which the process of Hofmann and Wulff⁴⁶ is applied. The oil is purified by treatment with hydrogen chloride in an organic solvent.

4636. The insoluble substances in the product of hydrogenation of coal are separated from the crude oil by the addition of naphthalene or like hydrocarbon. An absorbent such as fuller's earth may be added.⁴⁷

4637. The distillation of (*inter alia*) solid or liquid residues of hydrogenation is attended with considerable loss.⁴⁸ This loss may be reduced by admitting at temperatures above

^{44a} I. G. Farbenind. A.-G., Brit. Pat. 314,405, Jan. 23, 1928; *Chem. Abst.*, **1930**, 1534.

^{44c} I. G. Farbenind. A.-G., French Pat., 661,327, Oct. 1, 1928; *Chem. Abst.*, **1930**, 490.

^{44d} I. G. Farbenind. A.-G., Brit. Pat. 309,229, Oct. 3, 1927; *Chem. Abst.*, **1930**, 489.

^{44e} Brit. Pat. 323,791, Sept. 11, 1928, to I. G. Farbenind. A.-G. Addition to Brit. Pat. 312,791; *Brit. Chem. Abst.*, **1930**, 310.

^{44f} I. G. Farbenind. A.-G., Brit. Pat. 315,764, July 17, 1928; *Chem. Abst.*, **1930**, 1725.

⁴⁵ *Brit. Chem. Abst.*, **1929**, 45B; French Pat. 623,184, Oct. 15, 1926, to Soc. Internat. des Combust. Liq.

^{45a} I. G. Farbenind. A.-G., French Pat. 661,740, Oct. 4, 1928; *Chem. Abst.*, **1930**, 492.

^{45b} I. G. Farbenind. A.-G., Brit. Pat. 304,404, Nov. 5, 1927; *Chem. Abst.*, **1929**, 4802.

⁴⁶ Brit. Pat. 298,484, convention date, Oct. 6, 1927, *Brit. Chem. Abst.*, **1930**, 406B. *cf.* para. 5037A.

⁴⁷ French Pat. 639,240, Aug. 9, 1927.

⁴⁸ Brit. Pat. 301,130, Sept. 5, 1927, to the I. G.

300° C. and under reduced pressure, gases or vapors which contain liquids of lower boiling-points (e.g., water, benzene, toluene, alcohol, benzine) preferably in a state of mist. The method is applicable to the distillation of the residues of berginized lignite.⁴⁹

4637A. For the recovery of organic substances which are volatilizable at an elevated temperature, a mixture of oleaginous liquors and solid matter obtained by destructive hydrogenation of coal is fed in a thin stream on to a revolving vertical cylinder or cone down the surface of which it flows.^{49a} The cone is heated by burner gases either from the outside or through a chimney within the cone, the gases passing in the latter case down the inside of the cone and up over the outer surface. The volatile products are carried off by the heating gases, and the solid residue is removed by suitably placed scrapers.

4638. Apparatus for destructive distillation with cracking and hydrogenation of product. (Raw materials are coal, shale, lignite, distillation residues, resin, pitch, etc.)⁵⁰

4638A. Destructive hydrogenation of coal in suspension in oil is effected in a vertical tower. A heavy oil not readily decomposed during the reaction, such as the product of a previous hydrogenation, is used to fill the tower, and the carbonaceous material is admitted at the top or bottom of the tower and hydrogen at its bottom, while the residual material is removed at its base by a pump. Temperatures of 300°–500° and a pressure of 100 atmospheres are suitable. Brit. Pat. 309,258 specifies various structural details.^{50a}

4638B. It is also proposed to distil solid carbonaceous material in oil by causing the comminuted material to move through a body of oil so as to be subjected to progressively increasing temperatures. Superheated steam, hydrogen or a gas containing hydrogen may be introduced at the hottest part of the oil so as to increase the yield of oil and to agitate the charge.^{50b}

4638C. Operating pressures ranging from 300 to 1000 atmospheres have been proposed by Gordon.^{50c} When the pressure range is between 300 and 500 atmospheres a temperature of 420° C. is preferred while somewhat higher temperatures are considered desirable with the higher pressures.

4638D. Not many years have elapsed since technical men in general regarded pressures of a few hundred pounds rather hazardous in the conduct of chemical operations. This is in contrast with the recommendation by Gordon^{50d} that pressures running from 1000 atmospheres up to even as high as 10,000 atmospheres be used. By one procedure employing such pressures the material to be hydrogenated is treated with circulation of hydrogen and a final treatment is then accorded with a single passage of hydrogen.

4638E. Solid carbonaceous material, such as coal or lignite, which on treatment at raised temperatures with hydrogen under 200 atmospheres pressure yields a viscous product, is treated (with or without addition of an oil or tar vehicle) with hydrogen under a pressure of at least 500 atmospheres and a temperature of approximately 420° to yield a mobile product which can be filtered.^{50e}

4638F. Apparatus^{50f} for the treatment of a mixture of brown coal and a high-boiling coal hydrogenation product.

4638G. Recovery of hydrogenation products.^{50g}

⁴⁹ *Chem. Age* (London), 1929, 19, 638.

^{49a} I. G. Farbenind. A.-G., Brit. Pat., 317,506, April 30, 1928; *Brit. Chem. Abst.*, 1929, 879B.

⁵⁰ Brit. Pat. 132,490, June 4, 1919, to Rousseau; *Chem. Abst.*, 1920, 341.

^{50a} Humphrey and Imp. Chem. Ind., Ltd., Brit. Pat. 308,995, Nov. 30, 1927; *Chem. Abst.*, 1930, 490; for structural details see Brit. Pat. 309,258.

^{50b} Humphrey and Imp. Chem. Ind., Ltd., Brit. Pat. 305,744, Nov. 30, 1927; *Chem. Abst.*, 1929, 5032-3.

^{50c} Gordon and Imp. Chem. Ind., Ltd., Brit. Pat. 309,095, Dec. 2, 1927; *Chem. Abst.*, 1930, 490.

^{50d} Gordon and Imp. Chem. Ind., Ltd., Brit. Pat. 309,239, Jan. 14, 1928; *Chem. Abst.*, 1930, 490.

^{50e} Rule and Imp. Chem. Ind., Ltd., Brit. Pat. 314,213, June 22, 1928; *Chem. Abst.*, 1930, 1204.

^{50f} I. G. Farbenind. A.-G., Brit. Pat., 322,489, Sept. 3, 1928; *Chem. Age* (London), 1930, 125.

^{50g} Luther and Pieroh, Assrs. to I. G. Farbenind. A.-G., U. S. Pat. 1,723,458, Aug. 6, 1929; Ger. Pat., Nov. 27, 1925; see Brit. Pat. 262,086; *Brit. Chem. Abst.*, 1928, 151B; 1929, 917B.

liquid products are condensed out of the gases, and the remaining gases are then scrubbed with a benzine obtained by the destructive hydrogenation. The dissolved gases are liberated by reduction of pressure or increase of temperature. The hydrogen, which is first obtained [which is the first to come off] is compressed and used again.⁵⁴

4643A. Gaseous mixtures containing hydrogen are washed under pressure and at elevated temperatures with a liquid consisting of a tar or mineral oil, the solvent power of which for hydrogen increases with a rise of temperature. On cooling the liquid without releasing the pressure, a gas rich in hydrogen is evolved. Suspensions of coal in oil, or tars which are to be hydrogenated, may be used as washing liquids under such conditions of temperature and pressure that they take up the quantity of hydrogen necessary for their subsequent hydrogenation, without any appreciable alteration in their chemical nature.⁵⁵

4644. Another method⁵⁶ seems directed towards a vigorous purification of the hydrogen and is perhaps intended for the ammonia synthesis rather than for the less exacting process of berginization. The gaseous mixtures are washed with benzines under pressure and at a temperature below -60° but above the freezing-point of the solvent. Greater efficiency is obtained by atomizing the solvent in a scrubber into which the gas is introduced under pressure. Methane and its higher homologs are the chief impurities removed, other compounds being potential catalytic poisons such as ether, carbon monoxide, hydrogen sulphide, carbon disulphide, etc.⁵⁷

4645. This preparation for ammonia synthesis is the express object of the process described below.⁵⁸ The accumulation of methane in the residual gases can be avoided, but nitrogen continues to accumulate. The gases are particularly suitable for ammonia synthesis owing to their low sulphur content.

4645A. The unsaturated hydrocarbons in gaseous mixtures obtained by the thermal treatment of gases containing hydrocarbons are recovered by adsorption under pressure on activated carbon or other solid absorbent. The residual compressed gas, principally hydrogen, is utilized in the hydrogenation of coal.⁵⁹

4646. Purification of Gases by Liquefaction.⁶⁰ "Hydrogen is recovered from admixture with methane and other light hydrocarbons and catalyst poisons by cooling to temperatures above the liquefaction point of hydrogen and below that of the other constituents at a pressure above atmospheric, washing the gas by the liquid condensate thus produced and finally passing it through a highly porous substance, which may be precooled, e.g., by the liquid condensates. Washing with other organic materials such as alcohols or ketones may be combined with the washing with the condensates. The porous mass may be active charcoal, silica or alumina gel, chabasite or lignite."⁶⁰

The impure hydrogen, containing about 8 per cent of methane (and homologs) and small quantities of potential catalyst poisons, is washed at -150° and at a pressure up to 400 atmospheres with a suitable organic solvent, of which liquid methane, obtained in the process, is preferred. Final traces of the impurities are removed by adsorption in active charcoal, silica, alumina gel, natural substances like chabasite, brown coal, etc., either separately or together. The hydrogen remaining is exceptionally pure and particularly suitable for the synthesis of ammonia. The liquid methane and cold hydrogen may be used to precool the impure gas and the adsorbents. When methane has been used in the preliminary washing the adsorbent is sufficiently regenerated by raising the temperature to -80° .⁶¹

4647. Lander, Sinnatt and King,⁶² instead of purifying the whole of the circulating gas in berginization in each cycle, treat a portion only, sufficient to maintain a satisfactory composition. The treatment results in removing sulphur, carbon dioxide and hydrocarbons.

4647A. Hydrogen and gases containing hydrogen are rendered fit for reuse in hydrogenation by treating them with absorbents until the concentration of hydrogen sulphide is below

⁵⁴ *Chem. Age* (London), 1927, 17, 173; cf. French Pat. 634,821, May 21, 1927; *Chem. Abst.*, 1928, 22, 3979.

⁵⁵ I. G. Farbenind. A.-G., Brit. Pat. 325,968, Jan. 30, 1929; *Brit. Chem. Abst.*, 1930, 449B.

⁵⁶ Brit. Pat. 299,167, Nov. 29, 1927, to Johnson (an I. G. communication).

⁵⁷ *Brit. Chem. Abst.*, 1929, 46B.

⁵⁸ Brit. Pat. 302,620, Sept. 17, 1927, to Johnson (an I. G. communication).

⁵⁹ Brit. Pat. 325,309, Nov. 26, 1928, to Johnson, from I. G. Farbenind. A.-G.; *Brit. Chem. Abst.*, 1930, 406.

⁶⁰ Brit. Pat. 299,588, Sept. 29, 1927 (an I. G. patent).

⁶¹ *Ill. Off. J.*, Dec. 19, 1928; *Univ. Oil Prod. Co. Bull.*

⁶² *Brit. Chem. Abst.*, 1929, 18B.

⁶³ Brit. Patent 302,629, Sept. 17, 1927.

0.3 per cent by volume. Fractions containing sulphur-fixing agents may be used as absorbents.^{62a}

4648. Berginization: Increasing Activity of Gases.⁶³ Gases capable of increasing the proportion of atomic hydrogen, carbon monoxide or other highly active gases.⁶⁴

PRODUCTS

PRIMARY PRODUCTS

4649. The diagram (Fig. 103) which is based on statements made by Bergius^{64a} at the Pittsburgh Conference, 1926, shows the products and yields obtained on berginization of a typical coal.

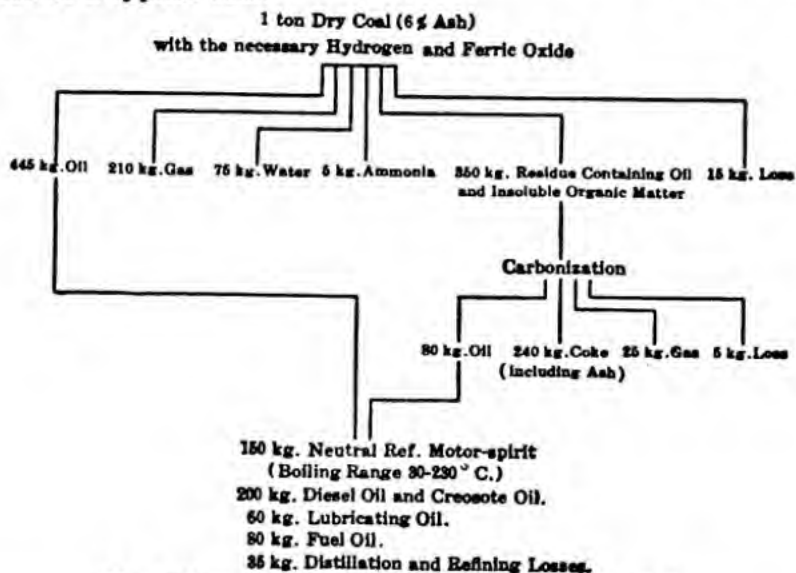


FIG. 103.—YIELDS FROM A BITUMINOUS GAS-COAL.

4650. Lander⁶⁵ gives a typical example of the yields with the 1-ton per day continuous plant of the British Fuel Research station.

YIELDS PER TON OF COAL	
Hydrogen Consumed = 114 lb.	
Fraction	0°-175° C. = 83 lb.
Fraction	175°-230° C. = 208 lb.
Fraction	230°-270° C. = 197 lb.
Fraction	270°-310° C. = 105 lb.
Fraction	310°-360° C. = 208 lb.
Pitch	= 329 lb.
Gas benzine	= 42 lb.
Bergin gas	= 325 lb.
Unconverted coal	= 363 lb.
Water	= 179 lb.
Coal ash	= 161 lb.
Loss	= 154 lb.
Coal 2240 lb. + hydrogen 114 lb. = 2354 lb.	

^{62a} I. G. Farbenind. A.-G., French Pat. 668,668, Jan. 30, 1929; *Chem. Abst.*, 1930, 1725.

⁶³ French Pat. 606,897, Feb. 17, 1925, to Prud'homme.

⁶⁴ *Brit. Chem. Abst.*, Mar. 18, 1927, 180B.

^{64a} The Transformation of Coal into Oil by Means of Hydrogenation. Bergius, *Proceedings of the International Conference on Bituminous Coal*, Nov., 1926, Carnegie Institute of Technology. See also *Ind. & Eng. Chem.*, News Edit., Dec. 10, 1926.

⁶⁵ *Chem. Age* (London), 1929, 20, 120.

4651. Bergius (*loc. cit.*) states that the hydrocarbons obtained are aliphatic, aromatic and hydroaromatic. The gasoline behaves, in internal combustion engines, like a mixture of natural gasoline and benzol. The production of satisfactory lubricating oils involved many difficulties, but this problem has now been solved in the laboratories of the Gesellschaft für Teer-Verwertung. The phenolic compounds consist chiefly of cresols. Fifty per cent of the nitrogen of the coal is obtained as ammonia, the remainder as organic bases. The sulphur is entirely converted to hydrogen sulphide. Bergius emphasizes the essential difference between the products of berginization and the tars of carbonization at any temperature, high or low. From 15 to 20 per cent of the carbon appears as methane and ethane.

4652. Tars and Oils from Berginized British Coals. Sinnatt, King and Linnell⁶⁶ report that from 50 to 60 per cent of average British bituminous coal may be converted into liquid hydrocarbons, while about 15-20 per cent is converted into gas and about 10 per cent of solid organic matter is found as a residue. Ormandy and Craven⁶⁷ have made, in association with the Fuel Research Division, a study of the light oils distilled from the crude oil obtained by the hydrogenation of a typical English bituminous coal, and the following is quoted from their paper: unsaturateds, 3.1 per cent by weight; aromatics: benzene 2.7, toluene 1.9 xylenes, etc., 2.9 per cent; paraffins, butanes, isopentane, etc., 10.8 per cent, *n*-pentane 10.5, per cent, isohexane, etc., 6.3 per cent, *n*-hexane 10.0 per cent, isohexane, etc., 2.9 per cent, *n*-heptane 6.5 per cent; naphthenes: cyclopentane 0.8 per cent, methylcyclopentane 4.5 per cent, cyclohexane 10.3 per cent, methylcyclohexanes 11.4 per cent; residue, 15.4 per cent.

4653. Oil from Lower Silesian Coal.⁶⁸ A detailed analysis was made of the oils obtained from unwashed coal dust containing 17.7 per cent of ash, 28.5 per cent of volatile matter (both reckoned on the dry coal), and an exceptionally high proportion of fusain, which is known to yield very little oil on berginization. The coal was made into a paste with half its weight of an oil obtained from a previous berginization of similar coal, and the experiment was run continuously for two and one-half days at a throughput of 7 kg. of paste per hour. The total oil yield was 36.45 per cent of the raw coal, i.e., 33.09 per cent of oily product and 3.36 per cent of benzene recoverable from the gas. The black, viscous oil contained 29.5 per cent of dust, to remove which the light oils were distilled off up to 230° (during which ammonium carbonate separated out in the receiver), and the residue was dissolved in benzene and filtered warm. After removing the benzene, the light and heavy oils were united and fractionally distilled (under diminished pressure above 220°) up to pitch (9.26 per cent of the raw coal). It is difficult to remove the oil completely from the dust, which, after extraction contained 40.65 per cent of ash and 10.45 per cent of volatile matter. The oil fractions were extracted by the usual methods for phenols, bases, etc., showing the total distillate to be composed of 75.7 per cent of neutral oils, 12.0 per cent of phenols, 3.5 per cent of bases, and small traces of carboxylic acids, resin, and a sediment. 10.3 per cent of the phenolic compound was phenol itself, while phenol, cresols, and xylenols (boiling-point up to 220°) constituted 66.5 per cent of the whole. The basic fraction contained primary (aniline, toluidine, xyldine), secondary (not identified), and tertiary bases (pyridine absent; collidine, quinoline, quinaldine, and probably isoquinoline identified). The benzene from the gas was refined with sulphuric acid and fractionally distilled, the bulk distilling below 185° and containing benzene, toluene, xylene (shown by nitration), with a large proportion of their hexahydro-derivatives (shown by dehydrogenation). The light oil fraction (boiling-point up to 180°) of the main product, similarly refined and fractionally distilled, had an analogous composition, the ratio of aromatics to hydroaromatics being, however, greater than in the benzene. The higher fraction (180°-220°) of the oil contained naphthalene and its tetrahydro- and decahydro-derivatives. All the neutral oil fractions were remarkable for their low sulphur content (0.76-1.12 per cent). Attempts to prepare a satisfactory lubricating oil from the higher fractions were unsuccessful. The solid constituents of the neutral oils comprised a small

⁶⁶ *J.S.C.I.*, Nov. 19, 1926, 392T.

⁶⁷ *J. Inst. Pet. Tech.*, 1926, 12, 77.

⁶⁸ Heyn and Dunkel, *Brennstoff-Chem.*, 1926, 7, 20, 81, 245.

quantity of paraffins and a considerable quantity of aromatic hydrocarbons (mainly phenanthrene).⁶⁹

4654. Oil from Lignite Semi-coke.⁷⁰ The oil obtained by Fischer and Frey from a German lignite semi-coke by treating 5–6 times for fifteen to sixteen hours at 460° with hydrogen under a maximum pressure of 200–260 atmospheres was examined. The yield of oil was 27 per cent of the coke. An analysis of the oil gave neutral oils (60°–150°) 8.9 per cent, (150°–280°) 38.2 per cent, (above 280°) 17.5 per cent; residue 17.8 per cent; phenol 3.2 per cent; *o*-cresol 1.5 per cent; *m*-cresol 1.9 per cent; phenols (220°–280°) 7.1 per cent (above 280°) 1.7 per cent; bases (180°–280°) 2.2 per cent. The products obtained by hydrogenation, viz., the cyclic nature of the hydrocarbons and the formation of phenols in quantity, furnish additional evidence of the aromatic structure of coal.⁷¹

4655. Oil from Arley Coal.⁷² Arley coal exposed for twelve hours to hydrogen at 430° and 127 atmospheres pressure absorbs 3.65 per cent of hydrogen, 67.6 per cent of the dry ash-free coal being converted into a liquid soluble in phenol and 61.4 per cent into a liquid soluble in chloroform. Of the hydrogen absorbed 2.3 per cent (reckoned on the coal) is fixed in the solid and liquid products, the latter containing also sulphur, nitrogen, and oxygen.⁷³

4656. According to Ger. Pat. 483,634,^{74a} a mixture of "gas" coal and "pitchy luster" coal in the proportions 100 : 40 yields the greatest amount of distillate on hydrogenation. The cracking of primary tar from a coal of Donetzki Basin at 380°–420° in presence of alumina and ferric oxide at 70 atmospheres initial hydrogen pressure gave a lower yield of low-boiling substances soluble in sulphuric acid and a higher yield of high-boiling fractions than in the absence of hydrogen. By alteration of cracking the aromatic content of the light products can be controlled.^{74b}

4657. Bergin Lubricants. Spilker,^{75c} dealing with synthetic lubricating oils, says that reduction products from berginizing coal and especially coal tar and coal-tar pitch show all the properties of the best lubricating oils. One of these, chrysene, is shown by analysis to have the composition $C_{18}H_{28}$ or C_nH_{n-8} . Lubricants from petroleum range from C_nH_{2n+2} , the paraffins, through C_nH_{2n} and C_nH_{2n-4} to about C_nH_{2n-6} . The lubricants obtained by hydrogenation of coal, coal tar, etc., are not constituted chemically like the heavy oils from petroleum. By suitable means they can be converted back to the aromatic compounds. This cannot be done with the constituents of the petroleum oils. The per-hydrogenated oils have a gravity of over 1; and range in viscosity Engler at 50° from 2 to 16, or even higher. This would call for the working out of new standards. Coal dust from the most recent coal formations combined with coal-tar pitch in the proportion of 2 : 1 forms the best raw material for the production of lubricants by berginization.

4657A. In order to obtain lubricating oils,⁷⁴ brown coal (or its fractions free from benzene or wax) is heated to 100°–200° with chlorides such as those of aluminum or iron suitable for use in the Friedel-Crafts reaction. As activating substances, there may be added uranyl nitrate or other salt of heavy metal of the sixth group, and the fractions may be preliminarily subjected to hydrogenation, oxidation or dehydrogenation.

⁶⁹ *Brit. Chem. Abst.*, 1926, 809B, see also Heyn, *Petroleum. Z.*, 1927, **23**, 281.

⁷⁰ Tropsch and Ter-Nedden, *Brennstoff-Chem.*, 1925, **6**, 143.

⁷¹ *J.S.C.I.*, **1925**, 486B.

⁷² Shatwell and Bowen, *Fuel*, **4**, 252.

⁷³ *J.S.C.I.*, **1925**, 530B.

^{74a} To Deutsch Bergin-A.-G. für Kohle und Erdölchemie, Apr. 2, 1927; *Chem. Abst.*, **1930**, 2275.

^{74b} Ipatiev, Petrov and Ivanov, *J. Appl. Chem. Russia*, 1929, **2**, 429–35; *Brit. Chem. Abst.*, **1930**, 309B.

^{74c} *Brennstoff-Chemie*, Sept. 1, 1926, 261.

⁷⁴ *Brit. Pat.* 316,701, May 11, 1928, to I. G. Farbenind. A.-G.; *Chem. Abst.*, **1930**, 1971.

4657B. Synthetic hydrocarbons of suitable viscosity, manufactured by hydrogenation of carbonaceous material, are mixed with small quantities (1 per cent or less) of organic acids containing more than five carbon atoms (*e.g.*, oleic acid), to form lubricating oils.⁷⁴

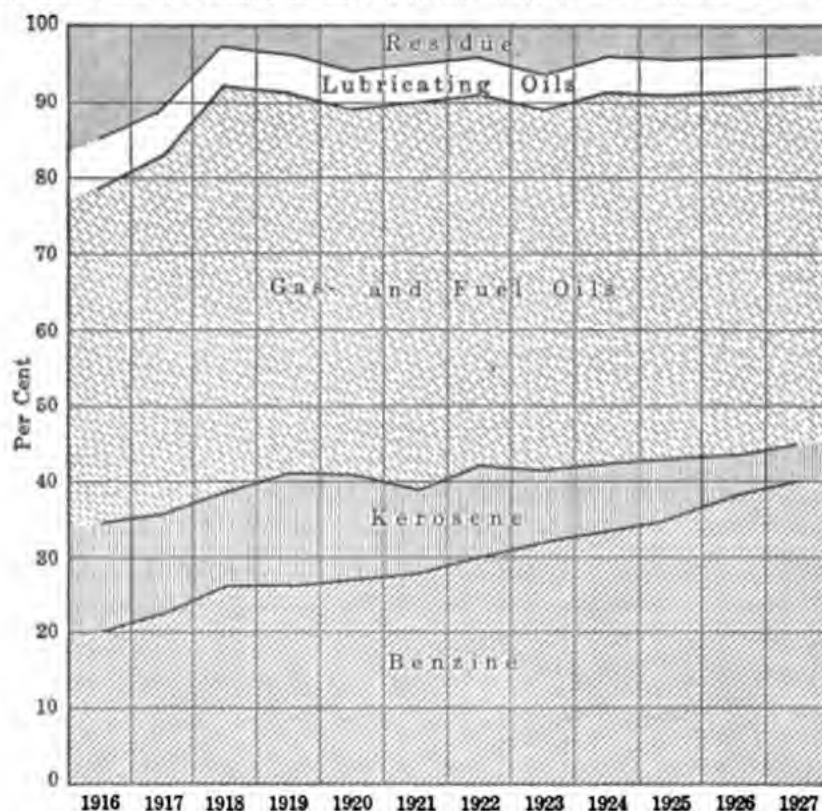


FIG. 104.—GRAPH INDICATING IN A GENERAL WAY THE NORMAL OR EXPECTED YIELDS FROM PETROLEUM SUBJECTED TO USUAL METHODS OF TREATMENT.⁷⁴

SECONDARY PRODUCTS

4658. Production of Aromatic Hydrocarbons. (a) Liquid hydrocarbons obtained from the destructive hydrogenation of carbonaceous materials are converted into products rich in aromatic hydrocarbons by heating them, either alone or together with water vapor or hydrogen, in the presence of dehydrogenating catalysts. Oxides of the metals of the sixth group of the periodic system, or mixtures of these with oxides of the metals of the third and fourth groups, form suitable catalysts. Active charcoal, either alone or mixed with these metallic oxides, may also be used for the purpose. (b) The above process may be applied to hydrocarbons resulting from cracking processes, or to any hydrocarbons containing cycloparaffins.⁷⁵

4659. Products of berginization are treated with excess of hydrogen under 10–200 atmospheres pressure at 500°–1000° C. in the presence of chromium or manganese oxide, for the production of benzene, naphthalene, anthracene and phenanthrene.⁷⁶

4660. Carbonaceous material is hydrogenated under pressure in presence of anthracene or a homolog above the decomposition temperature of hydrogenated anthracene. Anthracene, etc., may be recovered by fractional distillation of a part of the product. [Hofsäss, U. S. Pat. 1,711,499, May 7, 1929; *Brit. Chem. Abst.*, **1929**, 879B, *Cf.* paragraph 4720.]

⁷⁴ Wilke, *Brennstoff und Wärmewirtschaft*, 1929, Vol. 22, Wilhelm Knapp, publisher. Halle.

⁷⁵ Wells and Southcombe, *Brit. Pat.* 320,899, July 19, 1928; *Brit. Chem. Abst.*, **1930**, 134B.

⁷⁶ (a) *Brit. Pat.* 293,887 and (b) addition to 293,906, Mar. 10, 1927, to Johnson (an I. G. communication); *Brit. Chem. Abst.*, **1928**, 702B.

⁷⁶ *Brit. Pat.* 281,298; *Chem. Age* (London), 1928, **18**, 104.

4661. A similar process⁷⁷ is applicable to carbonaceous materials containing substantial quantities of non-aromatic hydrocarbons such as: coal,⁷⁸ tar, mineral oil, pitch, asphalt, resin, bitumen or their distillation or conversion products. The process can be accelerated by use of catalysts such as: aluminum hydroxide, charcoal impregnated with phosphoric acid, magnesia containing 1 per cent of ruthenium chloride, copper oxide with iron oxide, silver silicate, titanate acid, oxides of beryllium, of magnesium or of calcium. The products are aromatic, unsaturated aliphatic, and hydroaromatic hydrocarbons; they can be used in high-compression internal combustion engines, as they do not cause knock.⁷⁹

4662. Among the products to which the process of Brit. Pat. 303,761, Sept. 3, 1927, and Feb. 25, 1928, to Johnson (an I. G. patent) is applicable are products of berginization. This is a cracking process, using a hydrogen halide and as catalyst an activated metal with aluminum chloride.

4663. A cracking (non-hydrogenating) and synthetic process for the treatment of aliphatic hydrocarbons to produce olefines is described in Brit. Pat. 301,402, June 27, 1927, to Johnson (an I. G. communication). The process is applicable to products of berginization. The resulting unsaturated hydrocarbons may be polymerized to rubber-like compounds.⁸⁰

4664. Manufacture of [Rubber-like] Hydrocarbons of High Molecular Weight.⁸¹ Products, consisting substantially of 4-carbon olefines having at least two, preferably conjugated, double linkings, obtained from the destructive hydrogenation of coal, oils, etc., are polymerized to rubber-like compounds by treatment with metallic sodium, stannic chloride, carbon dioxide, etc., or by prolonged heating. Examples of suitable materials are the fraction, boiling-point about 100°, from hydrogenated mineral oil; isoprene from a hydrogenated coal fraction, boiling-point 30°–40°, which has been passed over chromium oxide at 500°, converted into amyl chloride by hydrochloric acid, passed at reduced pressure over barium chloride at 400° to give β -isoamylene, which is chlorinated and passed again over hot barium chloride; and butadiene prepared by cracking a hydrogenated coal fraction of boiling-point 65°–75°.⁸²

4665. The production of alcohols from the gases of berginization is effected in the following manner.⁸³ The gases are cracked or dehydrogenated and the resulting olefines are converted into alcohols by absorption in sulphuric acid, followed by hydrolysis. *Ex.* isopropyl and butyl alcohols from gases of berginized coal.⁸⁴

4665A. Hydrocarbon Derivatives Containing Oxygen or Sulphur. Difficultly condensable hydrocarbon mixtures, especially those of low molecular weight up to pentane which may be obtained by the destructive hydrogenation of carbonaceous materials, are treated with gases containing oxygen or sulphur, such as carbon dioxide, steam, air or hydrogen sulphide, at temperatures of 500°–800° and preferably in the presence of catalysts such as manganese dioxide, vanadium, molybdenum or chromium, manganese sulphide, alumina, active carbon or silica, elements and compounds of groups 1 and 2 of the periodic system or their mixtures; with or without use of pressure. Among the compounds which may be obtained are acetic acid and its homologs, ketones, acetaldehyde, alcohols, butadiene, butylene, propylene, thiophene, etc.⁸⁵

4666. Residual Gases.⁸⁶ The residual gases of berginization evacuated from the scrubbers are heated with catalysts to 450°–1000° C. for the production of liquid hydrocarbons. Water-gas, producer gas or ammonia may be added.

4666A. Gaseous hydrocarbons from the hydrogenation of coal are liquefied and fractionated to give a liquid which at 15° gives a pressure in a closed space of 10 kg. per sq. cm., and which is used for lighting.⁸⁷

4667. Motor Fuel Mixtures.⁸⁸ The use of mixtures of berginization products, gasoline, methanol, benzene, etc., is proposed as fuel for internal combustion engines.

⁷⁷ Brit. Pat. 302,253, June 9, 1927, to Johnson (an I. G. communication).

⁷⁸ *Sic*, though it is said later that the raw material is to be a liquid or a gas.

⁷⁹ *Chem. Age* (London), 1929, 20, 81.

⁸⁰ *Chem. Age* (London), 1929, 20, 12.

⁸¹ Brit. Pat. 298,584, June 9, 1927, to I. G.

⁸² *Brit. Chem. Abst.*, 1928, 919B.

⁸³ Brit. Pat. 301,000, June 18, 1927, to Johnson (an I. G. communication).

⁸⁴ *Chem. Age* (London), 1928, 19, 638.

⁸⁵ I. G. Farbenind. A.-G., Brit. Pat. 305,603, Oct. 6, 1927; *Chem. Abst.*, 1929, 4802.

⁸⁶ French Pat. 639,243, Aug. 9, 1927, to Soc. internat. des combust. liq.

⁸⁷ Florentin and Kling, French Pat. 661,828, Jan. 25, 1928; *Chem. Abst.*, 1930, 1204.

⁸⁸ Brit. Pat. 259,944, Oct. 19, 1925, to the I. G. Farbenind. A.-G.

4668. Other patents for use of bergin-benzine are: Brit. Pat. 287,115, Nov. 9, 1925, to I. G. Farbenind. A.-G. Bergin-benzine in oil varnish thinners. 287,116, same date, same patentee, same product in lacquers. 287,114, same date, same patentee, same product in soaps. 278,341, Oct. 2, 1926, same patentee, same product in motor fuels with aliphatic alcohols and natural benzine. The bergin-benzine is readily miscible with the lower alcohols. Reference is made to Brit. Pat. 259,944. 261,039, Nov. 9, 1925, to same patentee, for use as solvents, for dry cleaning, for dissolving rubber, for lacquers, shoe and floor polishes, detergents, etc. Also mixed with methanol, as fuel for internal combustion engines.⁸⁷

4668A. The hydrocarbons obtained by the destructive hydrogenation of coal, oil, shale, etc., are converted into products of higher boiling point and increased viscosity by treating them with halogens or compounds yielding halogen, with the addition of an element from groups 3-8 which is capable of existing in metallic form, or compounds of mixtures of these. The halogens or halogen compounds may then be removed and the products further condensed.^{87a}

4668B. A paste of coal and oil is hydrogenated under conditions, *e.g.*, at 410° and under 200 atmospheres which result in only a partial hydrogenation of the coal with the formation of a liquid product which solidifies on cooling to the ordinary temperature. This is used as a binding agent for briquetting fuels, particularly friable semi-coke.^{87b}

EXPLOITATION

4669. Financial Aspects of Berginization. Late in 1927 an authoritative statement on the position and policies of the I. G. was published by the German

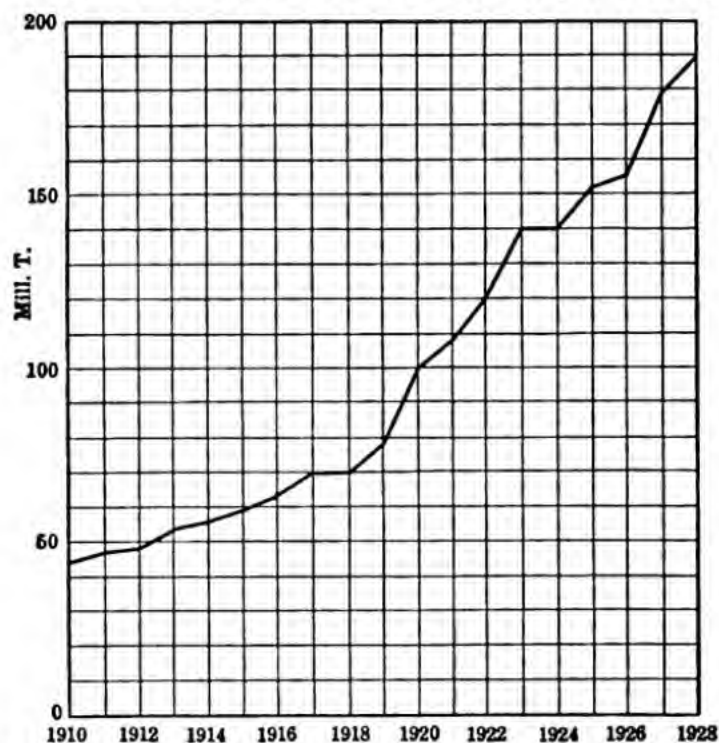


FIG. 105.—INCREASE IN THE PETROLEUM REQUIREMENTS OF THE WORLD DURING THE PERIOD 1910-1928.^{87c}

⁸⁷ Brit. Chem. Abst., 1928, 530B. Halogenation of bergin products and the like is described in Brit. Pat. 301,009, June 18, 1927, to Johnson (an I. G. communication).

^{87a} I. G. Farbenind. A.-G., Brit. Pat. 320,846, Appln. date, May 18, 1928; *Chem. Age* (London), 1929, 628.

^{87b} Imperial Chem. Ind., Ltd., and Slade, Brit. Pat. 322,194, July 31, 1928; *Brit. Chem. Abst.*, 1930, 132B.

banking house of Schwarz, Goldschmidt and Co., which, *inter alia*, dealt with the financial aspects of berginization. It says that one may estimate the cost of an installation which is intended to produce 50,000 tons of coal oil per year, with the necessary reserves, at about 8 million marks. The cost of production per ton of refined oils, consisting of benzine, motor oil, lubricating oil, heating oil and ammonia, etc., is calculated to be about 90 marks. It will be possible to reduce this cost to 70-75 marks, if the power is produced under modern conditions in the same plant. The average value per ton would vary between 140 and 190 marks on the basis of present prices according to the proportions in the mixture

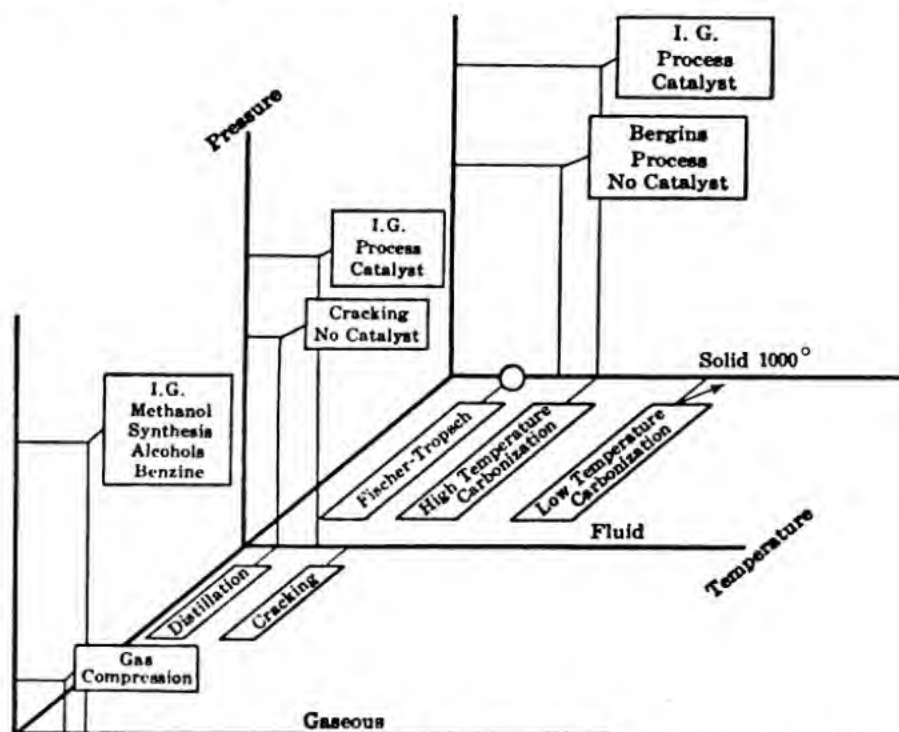


FIG. 106.—VARIOUS METHODS YIELDING AVAILABLE MOTOR FUELS.^{87c}

of the above-mentioned oil derivatives. This is from 50 to 100 marks higher than the production cost. Taking the average, an installation which produces 50,000 tons at a cost of about 80 marks per ton, and which sells the same quantity at 160 marks, makes a gross profit of 4 million marks.⁸⁸

4670. Gasoline Production by Berginization, 1928. The I. G. undertook to produce, in Germany, 100,000 tons of gasoline by berginization of lignite during 1928. In 1929 double that quantity was expected without expansion of the plant, owing to improved methods. Lubricating oils have been successfully produced and have proved satisfactory.⁸⁹

^{87c} Wilke, *Brennstoff und Warmewirtschaft*, 1929, Vol. 22, Wilhelm Knapp, publisher, Halle.

⁸⁸ *Chem. Age* (London), 1927, 17, 435.

⁸⁹ *Chem. Age*, (London), 1928, 18, 517.

4671. Liquefaction of coal, using brown coal, has been highly successful at the Leuna plant of the I. G.⁹⁰ A large plant for the treatment of anthracite will soon be in operation at the Mont Cenis mine. Plants are under construction in other countries, e.g., Hungary, and it is understood that the question of exploiting the Bergius process in South Africa is being studied.

4672. At Mannheim-Rheinau there was in 1926 a medium-sized pilot plant consisting of two units, each capable of treating 2 tons of coal in twenty-four hours. Two large plants had been erected in Germany. One of these is at Merse-

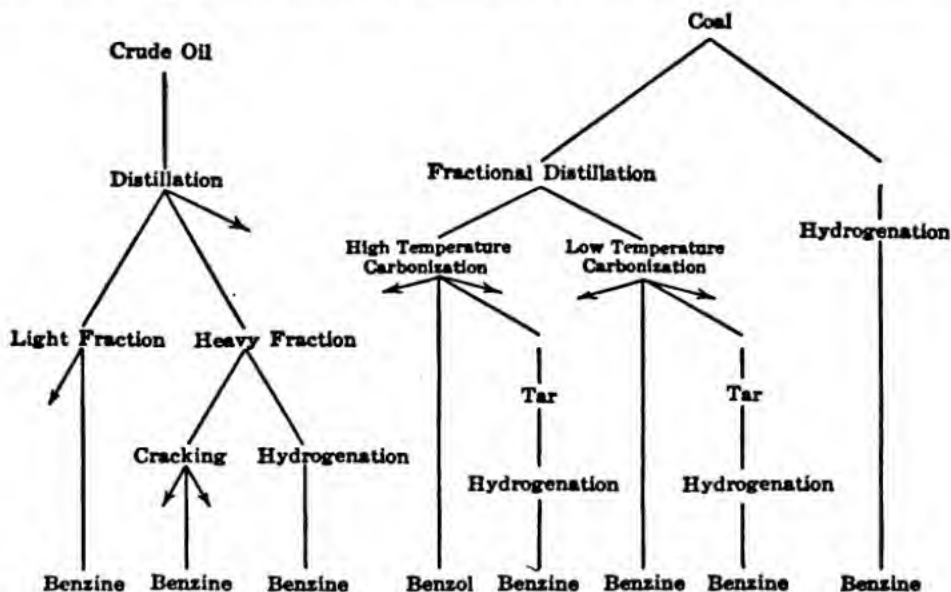


FIG. 107.—CONVERSION METHODS FOR THE TRANSFORMATION OF RAW FUEL MATERIAL INTO AVAILABLE MOTOR FUELS.^{90a}

burg in the heart of the lignite territory and is under the control of the dye-stuffs group, especially of the Badische Company. The other, belonging to the Gesellschaft für Teer-Verwertung is in the Ruhr district. The estimated yearly output of these is 1,000,000 barrels of oil products.

4672A. A method of improving the economy of operating a coke-oven plant by running a Bergius hydrogenation plant in co-operation therewith has been described as follows: The coke-oven gas poor in hydrogen, produced in the first stages of distillation, is mixed with the rich gas from the hydrogenation process, and distributed as illuminating gas in long-distance transmission systems. The gas rich in hydrogen evolved in the later stages of distillation is supplemented with hydrogen made by utilizing the coke, and used in the hydrogenation plant. A poorer gas coal is used in the coke-oven plant than in the hydrogenation plant.⁹¹

4672B. It has been suggested that the waste gases from the hydrogenation process, together with the vapors suspended therein, may be burnt as near as possible to the place of production and used as an engine fuel. The waste heat of the gases leaving the engine may be utilized in the hydrogenation process. The high pressure waste gases may also be utilized as they leave the apparatus in one or more machines of the turbine type. The hydrogen is

⁹⁰ *Chem. Met. Eng.*, 1928, 35, 644.

^{90a} Wilke, *loc. cit.*

⁹¹ Soc. Internat. des Combustibles Liquides, French Pat. 630,328, March 5, 1927; *Brit. Chem. Abstr.*, 1930, 131-2B.

then recovered from these gases by treating them with steam under pressure, and is returned to the hydrogenating vessel. The carbon dioxide thereby formed may likewise be allowed to expand in a turbine with the production of useful work.⁹²

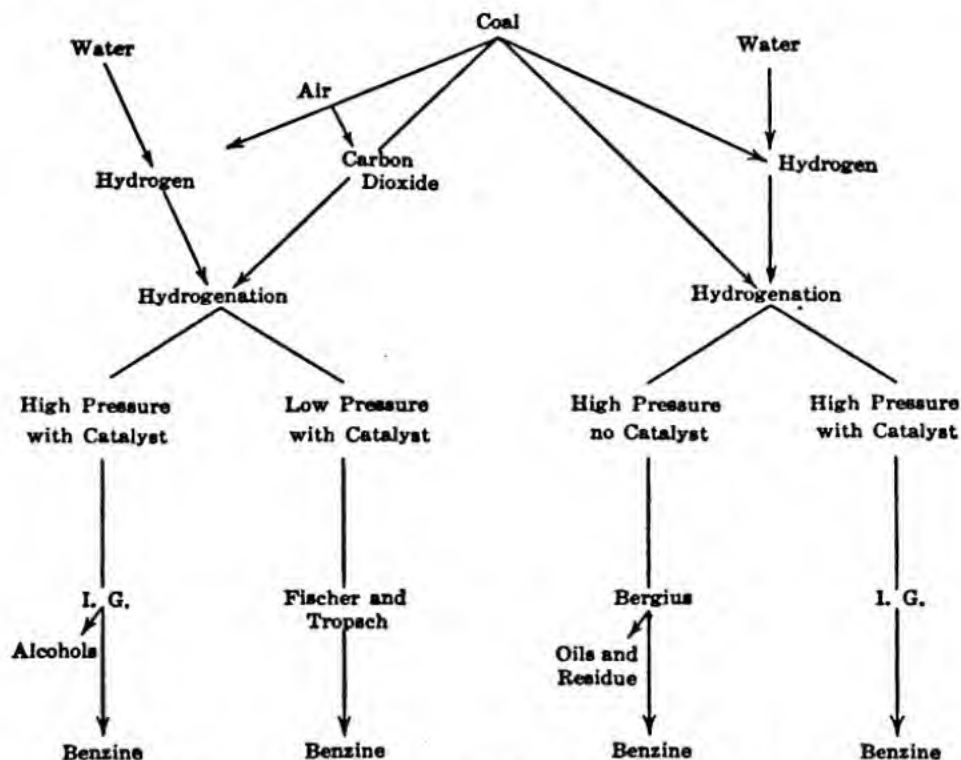


FIG. 108.—ROUTES OF CONVERSION OF COAL TO VOLATILE LIQUID FUELS.^{92a}

ADDITIONAL REFERENCES TO COAL LIQUEFACTION

4673. Berthelot. Chemical utilization of coal. *Chimie et industrie*, Spec. No. 166, Apr., 1928. An address on carbonization, liquefaction and gasification of coal.

4674. Bruckmann. Liquefaction of coal and world economics. *Petrol. Z.*, 1928, **24**, 26; *Mining J.*, 1928, **160**, 69, 94, 116; *Chem. Abst.*, 1928, **23**, 3279. Bruckmann figures costs at 71 marks per 1000 kg. treated, from which the products at German prices conservatively yield 141 marks or a surplus of 70 marks per 1000 kg. of coal. A plant to produce 50,000 tons of coal oil annually costs about 10 million marks. This means a conservative profit of 25 per cent on the capital cost of the plant. This would be increased for brown coal due to cheaper mining costs. Bruckmann suggests yearly construction of plants of 200,000 tons oil capacity. Thus up to 1932 construction will keep pace with the increase in demands; for a few years equilibrium will be established; after this importations will gradually decrease. To reach independence, Germany will require an investment of 500 million marks.

4675. Chaux. Combustible liquids from coal. *Bull. soc. chim.*, 1928, **43**, 385. A lecture reviewing the field. Bibliography of 160 references.

4676. Czermak. Utilization of coal. *Montan. Rundschau*, 1927, **9**, 283, 309, 337, 371. A comprehensive and, in some respects, a detailed review of modern methods of processing coal, including producer gas, berginization, low-temperature carbonization, synthol and synthin.

⁹² Swiss Pat. 123,928, Jan. 11, 1927, and Swiss Pat. 124,135, Jan. 6, 1927, to Giger; *Brit. Chem. Abst.*, 1930, 405B.

^{92a} Wilke, *loc. cit.*

4677. Dunston and Shatwell. Liquid fuels other than petroleum. *J. Inst. Petrol. Techn.*, 1928, 14, 64. Summary of information concerning the production of motor fuels by low-temperature carbonization, berginization, synthol and synthin processes.

4678. Daugherty. Hydrogenating low-grade coal in Germany. *Chem. Met.*, 1928, 214. Report by U. S. Trade Commissioner to Germany.

4679. Dyes. Conversion of lignite and coal into liquids and oils. *Chem. Ztg.*, 1927, 51, 853, 873. A general discussion of the commercial situation and advantages of the various processes. Detailed references to patent literature.

4680. Fieldner. Motor fuels from coal. *U. S. Bur. Mines Inform. Circ. No. 6075*, July, 1928. Some discussion of yields from other than berginization processes. Description of Bergius process and apparatus. Estimates cost in the United States of gasoline made by present process and plant as 40-50 cents per gallon at the refinery.

4681. Florentin. Synthesis of liquid fuels. *Chimie et industrie*, Spec. No. 228, Apr., 1928. A review of the various processes especially of berginization and Kling and Florentin's results.

4682. Furness. Synthetic motor fuels. *Ind. Chemist*, 1925, 1, 475. Discussion of several possible substitutes for natural gasoline. Furness considers synthetic methanol and liquid fuels produced by "some simple, catalytic gas reactions" are the most likely candidates. Seems to have ignored berginization.

4683. Fricke and Spiller. Hydrogenation under pressure [non-catalytic]. *Ber.*, 1928, 58, 1596. Apparatus and charts.

4684. Graham. The conversion of coal into oil by hydrogenation. *Colliery Guardian*, 1925, 130, 973. Review up to 1925.

4685. *Idem.* Conversion of coal into oil by treatment with hydrogen under high pressure. *Iron Coal Trades Rev.*, Diamond Jubilee Issue 87, Dec., 1927. A review and discussion.

4686. Graham and Skinner. The action of hydrogen on coal. *J.S.C.I.*, 1929, 129-136T, a critical review of experimental coal hydrogenation with and without catalysts. The work on which the article is based is that dealt with in paras. 4403-6, 4433-4, 4436, 4438-4444, 4447 and 4501. The greater part of the paper deals with the results obtained by British workers on British coals. These are elaborately set out in four tables showing: the analysis and classification of 34 coals used, the results of hydrogenation with and without catalysts, and the analysis of the solid products. Graham and Skinner believe that the application of catalysts greatly increases the probability of making coal liquefaction a commercial success. They estimate that, in Great Britain, about 10,000,000 additional tons of coal per annum would thus be utilized.

4687. Haslam and Ward. The Bergius process. *Mech. Eng.*, Jan., 1928, 26. An optimistic forecast of the commercial value of hydrogenation. Reference is made to the extensive hydrogenation plant at Mannheim using as raw material German brown coal or lignite. This is made into a paste with oil and treated with hydrogen at 1500 to 3000 pounds pressure. The lignite is largely converted into liquid products which, when distilled, give yields reported as follows: Fifteen per cent motor fuel (gasoline), 20 per cent Diesel oils, 6 per cent lubricants, 8 per cent fuel oil, and 20 per cent gas of high B.t.u. Haslam and Ward observe that this type of process "possesses distinct possibilities in reworking refinery residues into motor fuel."

4687A. Krauch. Catalysis applied to the conversion of hydrocarbons. *National Petrol. News*, July 24, 1929, p. 69; July 31, 72; Aug. 7, 75.

4688. Ludecke. Synthetic benzene. *Scienc. Ztg.*, 1928, 55, 6. Short summary of present situation of coal hydrogenation and fuel synthesis by reduction of carbon monoxide.

4688A. Naphthall. A review of the patents and literature on the Bergius and I. G. processes of coal liquefaction, methanol syntheses, and hydrogenation of hydrocarbons. The construction and heating of high-pressure reaction vessels are also reviewed, as well as recent progress in hydrogenation of petroleum. *Gas Wasserfach*, 1929, 72, 1178-84; *Chem. Abst.*, 1930, 442.

4688B. Nash. A review of the present status of the production of synthetic fuels. *Fuel Economy Review*, July 1, 1929.

4689. Nathan. Fuel for internal-combustion engines. *J.S.C.I.*, 1927, 46, 211T. An elaborate review of the actual and potential sources. Low-temperature carbonization berginization and water-gas synthesis regarded as likely soon to become important sources of liquid fuel supply.

4690. Passager. Notes on the (continuous) Bergius process. *Chimie et industrie*, Spec. No., 309, May, 1927. Brief general review and records of Passager's experiments in continuous berginization of coking coal, coal tar, etc., in general, confirmatory of other workers' results. Cf. para. 4806.

4691. Schuster. Bergius process for the liquefaction of coal. *Spawirtschaft*, 1925, **3**, 157; *Chem. Abst.*, 1926, **20**, 2573. Description (brief) of apparatus, operation and results of commercial berginization.

4692. Substitute motor fuels, a study of hydrogenation processes from the economic standpoint. *La Rev. Petrol.*, Feb. 8, 1930, p. 210. This paper states that one ton of coal treated

- (1) by the Bergius process yields 150 kg. of gasoline, 200 kg. of Diesel or impregnating oil, 80 kg. of fuel oil, 60 kg. of lubricating oil.
- (2) by the Patart, B.A.S.F., or Fischer and Tropesch method, 400-600 kg. of methanol, 200-600 kg. of liquid hydrocarbons.
- (3) by recovery of the gases from coke manufacture, 5-10 kg. of benzol, 5 kg. of ethyl alcohol, 5-7 kg. of methyl alcohol.

The Fischer process at the ordinary temperature requires very large plant. The apparatus for the production of synthetic methanol if much less cumbersome is not less costly.

CHAPTER XLVII

HYDROGENATION OF COAL AND RELATED HYDROCARBONS

IV.

OTHER PROCESSES FOR HYDROGENATION OF COAL AND COAL TARS¹

4700. In this era of enormous consumption of liquid fuels the development of hydrogenation processes for the conversion of coal into utilizable liquid fuels and the treatment of natural liquid fuels, that is, crude petroleum oil and shale oil, by hydrogen under various conditions to modify the properties of liquid hydrocarbons is making astonishing strides. The internal combustion motor of the automobile type, viewed collectively, consumes a tremendous amount of volatile liquid fuel. The public demand has grown for fuels of this character having improved anti-knock characteristics. Engines of higher compression are being adopted. This in turn results in greater economy in fuel. As a means of conserving the fuel supplies of the world the tendency in the direction of increased compression is a desirable and perhaps important one. The so-called anti-knock gasoline with which the public is thoroughly familiar, and demands even to the extent of paying a somewhat higher price for it, instead of the detonating type of gasoline previously used, has become an established commodity.

From the hydrogenation of coal, liquid fuels of excellent anti-knock characteristics can be obtained. While at the present time the cost of making such anti-knock fuels is greater than in the case of the usual methods of production of anti-knock gasoline from petroleum oils, the fact that such products can be obtained is comforting to those who keep in mind the welfare of future generations. Moreover, from heavy petroleum oils hydrogenolysis permits the production of fuels whose anti-knock value is extraordinarily high, not infrequently exceeding benzol in this respect.

Another development which is making rapid progress is the light-weight Diesel engine. Engines of this kind have been used successfully in airplanes as well as in trucks, buses and other vehicles of land travel. The Diesel engine operates best on a fuel which is of the detonating type. The versatility of the hydrogenation process is shown by the ability to obtain with it on the one hand a detonating fuel especially adapted for the Diesel engine, and on the other hand an anti-knock fuel highly appropriate for the ordinary automobile motor. With such a prospect confronting the inventive world it can be readily understood that the imagination of investigators and inventors everywhere has been stirred to unusual activity, resulting in a tremendous number of proposals, patents, plant lay-outs and mixed fuel products of various kinds. It is impossible in this volume to enter into detailed discussion of many of these, but effort has been made to present at least in very brief form some reference to most of this work. The present chapter includes a variety of such proposals.

4700A. The Brutzkus Method.² The equation of van't Hoff, $d\ln K/dT = Q/RT^2$, is expressed as follows: "Any chemical reaction can be directed and accelerated in a certain direction by continuous and simultaneous external variations in pressure, temperature and concentration, acting in a direction contrary to that of the corresponding variations caused by the desired reaction." Brutzkus suggests that the desired variations in pressure, temperature and concentration can easily be obtained by operating in a compressor constructed and operated substantially as a Diesel engine. The application of such a method for cracking or hydrogenation under various conditions (exothermic and endothermic reactions), for the treat-

¹ Some overlap is inevitable between the field covered in this chapter and that dealt with in Chapter XLIX.

² *Chimie et Industrie*, 1925, 14, 171 and 358; *Chem. Abst.*, 1926, 20, 102.

ment of petroleum, tar oils, turpentine, fats, sugars and molasses, cellulose compounds, and coal and for the synthesis of light oil from carbon monoxide, carbon dioxide and hydrogen is discussed, and compared with corresponding processes at present in use or proposed.

4701. Bianchi and Guardabassi² describe a more than unusual process and apparatus for the "cracking, catalyzing, and hydrogenation of carbonaceous materials." The raw materials may be mineral grease, oils, tar, naphtha, ground coal, etc. The material is passed continuously through a heated retort in the presence of catalysts. Revolving agitators produce a dust through which the reducing gases pass and on which they act. They then pass through a screen of chains, which may be coated with catalyst and may be shaken.

4702. The following description from Bianchi and Guardabassi's earlier patent⁴ is more detailed: An apparatus for treating oils, tar, naphtha, schists, ground coal and like materials at atmospheric pressure comprises a series of heated troughs provided with agitators for agitating material passing through the troughs; the latter are also provided with reticulated screens from which chains depend which may be vibrated by the revolving agitators. The chains and other parts of the apparatus contacting with the vapors may be coated with a catalyst such as reduced nickel, magnesia, iron oxide, copper oxide or other suitable metal oxide mixed with silicate jelly or nickel oxide or nitrate or powdered glass may be incorporated with a suitable varnish or thin gummy substance. Various other structural details are described. The process is particularly adapted for carrying out the process described in paragraph 4701, in which the chains serve to retain in the reaction chamber dust and carbon formed by decomposition of vapors of the carbonaceous materials under treatment, and hydrogen may be used for hydrogenating with nickel as a catalyst or removal of hydrogen may be effected by a catalyst such as magnesia or iron oxide.⁵

4703. Partial Conversion of Coal into Light Hydrocarbons. Finely pulverized coal is conveyed, suspended in a current of gas, e.g., steam, hydrogen, or coal gas, through a distilling apparatus heated to a suitable temperature.⁶

4704. Jolicard⁷ states that aromatic hydrocarbons are produced when coal is treated at 400° C. with nascent hydrogen in a furnace, which is not heated externally. The hydrogen may be produced for example by introducing a mixture of superheated steam and air at 500° C.; or carbon monoxide (producer-gas, water-gas) at 600° C. may be used in place of all or part of the air. A gaseous catalyst, such as chlorine or hydrochloric acid, may be introduced, or a solid catalyst, such as copper or nickel, may be deposited on the coal.

4704A. Fohlen^{7a} describes a process of destructive hydrogenation, whereby light hydrocarbons are obtained from natural or industrial fuels and carbonaceous materials by simultaneous cracking and treatment with nascent hydrogen under pressures from 5 atmospheres to superpressures and at temperatures from 200° C. to 1000° C. The nascent hydrogen is produced by the decomposition of hydrogen-containing bodies. In an example, water is used as the source of hydrogen; shale oil distilling from 260° C. upwards is stirred with an aqueous solution of metal halides, iron filings and copper or brass shavings for 4 hours at 300°-400° C. and 120-180 atmospheres pressure. The product yields 50 per cent of light oil of density 0.850 distilling below 200° C. and 42 per cent of oil of density 0.870 distilling between 200° C. and 300° C. Similar results are obtained by the use of temperatures of 500°-600° and pressures of 20-30 atmospheres.

4705. Hydrocarbons from Brown Coal.⁸ Hydrogen, obtained by passing steam over heated iron turnings, is passed through a vertical retort containing brown coal or similar material. The products are passed directly through a filtering tower to condensers and gas storage or may be passed through a retort containing more iron turnings. In the latter case from 25 kg. of brown coal, 20 kg. of heavy benzine, 0.5 kg. of carbon, and 5 cu. m. of gas can be obtained. If the treatment of the mixed vapors with iron turnings be omitted, 10 kg. of heavy benzine, 15 cu. m. of gas, and 3 kg. of carbon residue are obtained.⁹

4706. Bates¹⁰ describes a process and apparatus for making, from a mixture of coal and liquid hydrocarbon, a product suitable for use as fuel in semi-Diesel engines. Finely divided

² Brit. Pat. 278,041, May 27, 1926; *Chem. Age* (London), 1927, 17, 418.

⁴ Brit. Pat. 277,404, June 8, 1926.

⁵ *Chem. Abst.*, 1928, 22, 2654.

⁶ French Pat. 591,958, Mar. 11, 1924, to Comp. des Mines de Vicoigne, etc.

⁷ French Pat. 475,433, Feb. 17, 1914; *J.S.C.I.*, 1916, 36.

^{7a} Brit. Pat. 313,963, June 20, 1928; *Univ. Oil Prod. Co., Bulletin*.

⁸ Brit. Pat. 214,940, Aug. 24, 1923, to Linnmann.

⁹ *Brit. Chem. Abst.*, 1924, 778B.

¹⁰ Brit. Pat. 281,240, Oct. 31, 1927.

coal is mixed with a liquid hydrocarbon and subjected to intensive attrition in the presence of hydrogen. The temperature is maintained above the normal but below 300°; the pressure is not allowed to rise above 10 atmospheres. The heat required may be partially or wholly generated by the friction of the grinding mechanism.¹¹

4707. Coal and Oil: Exchange Hydrogenation. Lamplough and Hodgson¹² describe a process which seems to depend on a dehydrogenation of a mineral oil with hydrogenation of coal. From 10 to 50 per cent by weight of finely divided coal is mixed with a heavy mineral oil in such a manner that a stable dispersion of coal in oil is formed. The suspension so formed is subjected to high temperature (500°–600°) and pressure (100–600 lb./in.²), and the liquid fractionally distilled. The oil is apparently dehydrogenated by the coal, and the process may be carried to such an extent that the coal, with the exception of the ash, goes almost completely into the liquid state. The heaviest distilled fractions may be used as a binder in the manufacture of briquettes. Fractional condensation of the oil vapors may be effected and the distillation vapors may be hydrogenated and redistilled for spirit.¹³

4708. Liquefaction of Coal without Added Hydrogen. Herbst¹⁴ states that when lignite is heated with tar, the tar is cracked and used up. It appears possible to produce gases and gasoline by heating together low-temperature tar and lignite coke.

4709. Powdered Coal: Distillation with Hydrogenation. Gaertner¹⁵ injects powdered coal into a coking retort by use of combustion gases. Hydrogen or water-gas may be introduced into the retort and a finely divided metal catalyst may be used.

4710. Metallic Hydrides as Hydrogen Carriers. One process¹⁶ combines distillation and hydrogenation in an unusual fashion. The solid raw material is maintained in suspension in a stream of hot gas. This hot gas may be a reducing gas or (1) hydrogen, or (2) a substance yielding hydrogen, may be introduced into it. Among the substances named in class (2) are: calcium hydride, sodium hydride, formic acid and steam.

4711. Hugel, Paul and Boishel¹⁷ also use hydrides of alkali and alkaline earth metals in the hydrogenation of coal and petroleum hydrocarbons at temperatures below 300° C. and at pressures of about 100 atmospheres. The process is said to be immune to poisoning.¹⁸

4712. High-frequency Field in Hydrogenation of Coal. Uhlmann¹⁹ subjects a pulp of coal and water to the action of a high-frequency field. Hydrogen is supplied by an external source or by decomposition of the water.

4713. Process of Liquefying Carbon [Coal]. Liquids suitable for making fuels and lubricating oils are obtained from coal, lignite, or like solids by heating at atmospheric or higher pressure in a protective atmosphere with metal catalysts having melting-points lower than the reaction temperature. Water, mineral oils, tar oils, or other oils may be added to the coal, etc., and the mixture sprayed or atomized by hydrogen, methane, steam, or other hydrogen-containing gases into a vessel containing tin or tin alloys and preferably tin-lined. A temperature of 300°–600° is suitable. The operation may also be effected by heating a charge of coal and metal catalyst for several hours in a vessel filled with protective gas under pressure.²⁰

4714. In a later method Melamid²¹ prepares liquid products from coal, oils, tars, etc., by spraying the material mixed with a catalyst (e.g., finely divided metal, alloy or oxide) into a heated retort under pressure by means of a current of hydrogen or of hydrogen-containing gases.

4715. Trautmann²² treats the desulphurized vapors from coal distillation with hydrogenating gas in the presence of zinc, nickel, or tin in the form of powder or vapor. Superheated steam, water-gas, carbon monoxide, hydrogen, etc., may be added to promote hydrogenation.

¹¹ *Chem. Abst.*, 1928, 3517.

¹² *Brit. Pat.* 277,419, 1926.

¹³ *Brit. Chem. Abst.*, Dec. 7, 1927, 899B.

¹⁴ *Petroleum Z.*, 1926, 22, 947; *Chem. Abst.*, 1927, 21, 2378.

¹⁵ *Brit. Pat.* 281,110, Dec. 29, 1926.

¹⁶ *Brit. Pat.* 291,481, Jan. 20, 1927, to Haddon (from Kohlenveredlung A.-G.).

¹⁷ *Brit. Pat.* 286,206, Feb. 28, 1927.

¹⁸ *Chem. Age* (London), 18, 104 and 19, 627.

¹⁹ *Brit. Pat.* 283,177, Jan. 6, 1927; *Chem. Age* (London), 1928, 18, 225.

²⁰ *Brit. Pat.* 235,828, Sept. 5, 1925, to Melamid; *Brit. Chem. Abst.*, 1925, 700B.

²¹ *Brit. Pat.* 285,879, Feb. 24, 1927; *Chem. Abst.*, 1929, 23, 264. Cf. paras. 5034 and 5035.

²² *Brit. Pat.* 272,526, convention date, June 11, 1926; *Chem. Age* (London), 1927, 17, 173. Cf. para. 5015.

4716. Hydrogenation in the Arc. Coals, tar, mineral oils in fine division or vaporized are treated in the electric arc with water vapor in quantity less than half that necessary to produce water-gas. In this way from hard coal about 50 liters of acetylene is obtained per kilogram of coal. If the starting material is liquid the water vapor may be replaced by hydrogen, nitrogen, carbon dioxide or carbon monoxide. The materials are preferably preheated to a temperature short of decomposition.²²

4716A. Granular materials are heated by electrical resistance or arc heating while gases are forced through them to effect continuous agitation. Gaseous and low-boiling point olefins and diolefins are obtained from granular electrical conducting materials (such as coal which may be treated with gases such as hydrogen or tar or oil vapors).^{22a}

4717. Hydrogenation in arc under Liquid. Hansen²⁴ describes a process for the hydrogenation of hydrocarbons or coals by subjecting them to the action of an arc (or sparks from condenser discharge) the electrodes being immersed in a solvent for the products. One electrode may be of nickel and provided with a quartz sleeve for the passage of hydrogen.

4718. Hansen also treats coal and hydrocarbons with atomic hydrogen obtained by dissociating hydrogen by the arc or spark discharge. The process is exemplified in the treatment of naphthalene in the vapor phase.²⁵

4718A. Carboniferous material (e.g., coal) is hydrogenated with "nascent" hydrogen to produce liquid hydrocarbons. The material is kept within the temperature range at which the desired hydrocarbons are stable, in the region of the origin of the "nascent" hydrogen.^{25a}

4719. Feige's process comprises the combination of certain steps, viz., (1) coal is distilled; (2) part of the coke produced is burned to generate electricity for electrolysis of water; (3) the oxygen so produced gasifies the rest of the coke; (4) the gases so formed are hydrogenated by the electrolytic hydrogen, together with the tar and gaseous products of the original distillation.²⁶

4720. Unstable hydrogenated organic compounds, or those readily hydrogenated, have been proposed as hydrogen carriers.²⁷ Inorganic compounds, e.g., alkaline ferric oxide, or "lux," which catalyze the reaction may also be added. The readily oxidizable organic hydrogenated compounds are prepared as follows. Anthracene and solid potassium hydroxide are heated with hydrogen under pressure. At about 400° an active product is formed as a crystalline paste, which, on being distilled until the appearance of yellow fumes, yields 80-85 per cent of a hydrogenated anthracene. This product acts as a hydrogen carrier when heated with a "flaming" coal under 100 atmospheres pressure at 390° for ten minutes. The pressure falls and on cooling to 15° reaches a final value of 65 atmospheres. The yield is about the same as after heating for one hour, but the product with the shorter reaction time is of better quality and possesses a lower density and a smaller phenol content.²⁸

4720A. Coal is liquefied by heating under pressure of hydrogen with the addition of an alkaline oxide of iron consisting of oxide of iron 75-60 and sodium hydroxide 25-40 parts, and a small quantity of an alkaline earth carbonate.^{28a}

4721. Interchange Hydrogenation of Bituminous Distillates.²⁹ Products of the distillation of bituminous material, poor in hydrogen, are mixed with heavy petroleum distillate rich in hydrogen. On cracking the mixture, with or without a catalyst (such as aluminum or magnesium), the hydrogen is distributed evenly between the products, with the formation of low-boiling hydrocarbons.³⁰

4722. Almost the same is the following:³¹ The mixture of tar, asphaltum, etc., is cracked by heat in the presence of hydrocarbons rich in hydrogen so that the greater part of the

²² Brit. Pat. 286,825, Jan. 3, 1927, to Johnson (an I. G. patent); *Chem. Age* (London), 1928, 18, 346.

^{22a} I. G. Farbenind. A.-G., Brit. Pat. 313,756, June 23, 1928; *Chem. Abst.*, 1930, 1204. See also Brit. Pat. 268,599.

²⁴ Brit. Pat. 284,655, Feb. 2, 1927; *Chem. Age* (London), 1928, 18, 327.

²⁵ Brit. Pat. 234,224, Jan. 24, 1927; *Chem. Age* (London), 1928, 18, 305.

^{25a} Hansen, Swiss Pat. 132,904, Jan. 24, 1927; *Chem. Abst.*, 1930, 489.

²⁶ French Pat. 636,609, June 27, 1927.

²⁷ French Pat. 618,490 of July 5, 1925 to Société Internationale des Combustibles Liquides.

²⁸ *Brit. Chem. Abst.*, 1928, 117B. Cf. para. 4660.

^{28a} Soc. Internationale des Combustibles Liquides, Deutsche Bergin A.-G., für Kohle und Erdölchemie, French Pat. 667,993, Jan. 25, 1929; *Chem. Abst.*, 1930, 1494.

²⁹ Brit. Pat. 265,375, Feb. 3, 1926, to Braunkohlen-Produkte A.-G., Bube and Erlenbach.

³⁰ *Brit. Chem. Abst.*, 1927, 245B.

³¹ Ger. Pat. 432, 854, Feb. 1, 1924, to Braunkohlen-Produkte A.-G.

mixture consists of tar. The vapors of the mixture are heated in the presence of a metallic contact mass, preferably of aluminum, magnesium, or alloys rich in these metals. This results in an interchange of hydrogen equalizing the distribution of this element.²²

4723. Desulphurization and Hydrogenation of Lignite Tar Oils. Numerous methods for the removal of sulphur compounds from lignite tar benzine were tried by Fürth and Jaenicke. The non-success of methods used for the desulphurizing of mineral oils indicates that some of the sulphur compounds in lignite tar benzine are of a more stable nature, e.g., ring compounds, but attempts to separate thiophene were unsuccessful. Hydrogenation of lignite tar benzine containing different amounts of sulphur was carried out over finely divided nickel. In all cases the catalyst was gradually rendered inactive by the formation of a surface layer of nickel sulphide. By heating in oxygen and subsequent reduction the activity was regained. When nickel oxide was used, reduction to nickel and poisoning of the latter occurred simultaneously. The cost of purifying lignite tar benzine containing appreciable amounts of sulphur and unsaturated hydrocarbons sufficiently to render it available for use as a motor fuel is prohibitive.²³

4724. Hydrogenation of Aromatic and Coal-tar Hydrocarbons in Presence of Ferrous Oxide. Ramage²⁴ brings vapors of hydrocarbons of the benzene series mixed with vapors of non-aromatic hydrocarbons (e.g., mixed hydrocarbons from coal tar) together with steam at 550° C. in contact with ferrous oxide to produce a light fuel suitable for use in explosion engines.²⁵

4724A. A process, applicable to gas-oil, brown coal tar and similar products, which is a berginization with ferrous chloride as catalyst, is described by Terrisse and Dufour.²⁶

4724B. Fohlen^{26a} describes a process which consists essentially in cracking the raw material (coal, lignite, shale, tar, etc.), with addition of a catalyst (chiefly metallic chlorides) if desired, immediately purifying and desulphurizing the hot gases by passing over reduced metals of the same nature as used for the hydrogenation, and finally mixing with hydrogen and passing over a catalyst. The purifiers and desulphurizers are practically identical with the catalyst and may be considered as catalysts which are purposely "poisoned" to protect the catalyst proper; they generally work at a somewhat higher temperature (300°-250°) than the latter (250°-170°).

4725. Hydrocarbons and [Coal-tar] Phenols.²⁷ Aromatic hydrocarbons and phenols, contained in coal-tar fractions, are converted to lower homologs in the following manner: The vapors, with more than twice their volume of steam, are passed at 300°-500° C., or higher, over catalysts possessing both hydrogenating and dehydrogenating properties, e.g., nickel, cobalt, iron, copper, compounds of alkali, of alkaline earth or of earth metals, zinc and its compounds, and the difficultly reducible oxides of metals of Groups IV to VII, such as: titanium, vanadium, chromium and manganese.

4725A. Macnicol^{27a} has proposed to distil finely divided peat and the like, and heat the vapors under pressure with hydrogen, steam or water gas in presence of a catalyst. No specific catalyst is mentioned.

4726. Hydrogenation of Refined Tar-Hydrocarbons.²⁸ A Badische Co. process deals mainly with the refining of tar with steam and alkali, but the resulting hydrocarbons may be further improved by hydrogenation.²⁹ The tar is distilled with superheated steam over caustic soda or lime. The vapors are then passed with hydrogen over finely divided nickel, copper or iron at 100°-110° C.

4726A. Coal, tar or heavy oils are mixed with 5 to 25 per cent of lime or alumina and heated to about 1000° C. After this operation steam is passed through the hot coke and the combined mixture of gases, after purification, is hydrogenated at a pressure of 2 to 5 kg. per sq. cm. in presence of a catalyst.^{29a}

²² Brit. Chem. Abst., 1927, 182B.

²³ Z. angew. Chem., 1925, 38, 166.

²⁴ U. S. Pat. 1,439,976, Dec. 26, 1922; Chem. Abst., 1923, 17, 1131.

²⁵ For other uses of ferrous oxide in hydrogenation see U. S. Pat. 1,430,585, Oct. 3, 1922; also to Ramage; Chem. Abst., 1922, 16, 3903; and U. S. Pat. 1,687,890.

²⁶ Brit. Pat. 305,981, Feb. 13, 1928, to Terrisse and Dufour.

^{26a} Chimie & industrie, 1929, 21, 1141; Chem. Abst., 1929, 4553.

²⁷ Brit. Pat. 277,394, Mar. 13, 1926, to I. G. Farbenind. A.-G.

^{27a} Brit. Pat., 10,679, July 22, 1915.

²⁸ Brit. Pat. 249,309, Mar. 9, 1925.

²⁹ Chem. Age (London), 1926, 14, 358, 419.

^{29a} Andry-Bourgeois, French Pat., 564,148, March 21, 1923.

4727. Treatment of Low-temperature Tar from Lignite.⁴⁰ Part of this process applies to the hydrogenation of the light oils, in presence of a desulphurizing agent, to produce motor fuels.

4728. Hydrogenating Tar Oils. Dehydrated tar oil, suitably desulphurized, is hydrogenated at ordinary pressure by heating in shallow pans and bubbling in, in the presence of a suitable catalyst, coke-oven gas, which must necessarily be dry.⁴¹ A colloidal nickel catalyst may be used and the product may be deodorized and decolorized by treatment with superheated steam.

4729. According to Marchand such mixtures as tar and heavy oils with coke, sawdust, etc., briquetted, distilled at 200°–800° C. yield products which may, after cracking, be hydrogenated by passing through coke and iron turnings, accompanied by hydrogen generated by allowing water to fall on heated surfaces.⁴²

4730. The production of gases rich in olefines is effected by passing powdered or granular bituminous coal very quickly through a chamber at red heat and quickly separating the resulting gas from the carbon. This process also can be applied to tar oils, mineral oils, and their distillation residues, asphalts, and residues obtained by destructive hydrogenation of coal.⁴³

4731. Coke-oven Gas: Improvement of Caloric Value.⁴⁴ Schönfelder, Riese and Klempt have been able to raise the caloric value of coke-oven gas by an internal hydrogenation. The gas is passed successively over catalytic material at 700° comprising nickel precipitated on magnesite to destroy organic sulphur compounds and to break down heavy hydrocarbons, and, after removal of hydrogen sulphide, over pieces of clay containing reduced nickel at 420° to reduce carbon monoxide and carbon dioxide to methane and water by means of the hydrogen in the gas. The calorific value is raised, e.g., from 4136 to 5328 thermal units.⁴⁵

4731A. Hydrocarbon vapors from low-temperature distillation of coal are heated with hydrogen to produce gases of high calorific value and hydrocarbons of lower boiling point than the original hydrocarbons. Water-gas (or gas obtained by the high-temperature distillation of the coke obtained, with or without steaming, mixed with a gas containing hydrogen) is passed through coal heated to 600°–650° and the mixture of gases and vapors is passed to a cracking chamber, which may contain a catalyst, heated to about 750°, without intermediate cooling. The treated gases are then passed through a condenser, scrubber and purifying box.⁴⁶

4732. Preactivation of Hydrogen. One of the Prud'homme Company's patents describes production of petroleum and similar fuels by hydrogenation of the vapors obtained by distillation of materials such as lignite, peat, shales, tars, heavy oils, etc., in a chamber containing no catalyst. The hydrogen is rendered active by treatment with a catalyst in a separate chamber, fouling of the catalyst being thus avoided.⁴⁶

⁴⁰ French Pat. 596,143, July 3, 1924, to S. A. Hydrocarbures et Dérivés.

⁴¹ Brit. Pat. 236,230, June 26, 1925, to Demann; *Brit. Chem. Abst.*, 1926, 973B. U. S. Pat. 1,691,221, Nov. 13, 1928, to Bernhard and Demann.

⁴² Brit. Pat. 275,642, Aug. 5, 1926, by Marchand.

⁴³ I. G. Farbenind. A.-G., Brit. Pat. 320,211, Sept. 14, 1928; addn. to 301,775; *Chem. Age* (London), 1929, 532.

⁴⁴ *Ber. Ges. Kohlentechn.*, 1927, 2, 250.

⁴⁵ *Brit. Chem. Abst.*, 1928, 803B.

⁴⁶ South Metropolitan Gas Co., Evans and Stanier, Brit. Patent 306,435, Nov. 19, 1927; *Chem. Abst.*, 1929, 5033.

⁴⁶ *Brit. Chem. Abst.*, 1928, 438B; Brit. Pat. 275,585, July 12, 1927.

CHAPTER XLVIII

HYDROGENOLYSIS OF MINERAL OILS (I)

4800. In the preceding chapters mainly directed to the subject of hydrogenation of coal frequent reference has been made to the analogous hydrogenation of waxes, tar oils and certain other hydrocarbon oils, since much of the experimental work directed primarily to the conversion of coal has been compared with the results obtainable in the hydrogenation of normally liquid products. It has been difficult, therefore, in dealing with coal and mineral oil from this standpoint to follow a strict classification, hence Chapters XLVIII to L should be examined in conjunction with the four chapters preceding.

4801. The year 1912 was an active one with respect to pioneer work in the field of high-pressure treatment of mineral oils with hydrogen. Teodorin,¹ completing in 1911 an important research on this subject, undoubtedly was responsible for the instigation and stimulation of work by others in the same field. Teodorin used the classical hydrogenating catalysts on petroleum oils together with hydrogen pressures ranging in the neighborhood of 50 atmospheres and higher. He did not find nickel a suitable catalyst and attributes its lack of sustained activity to the poisoning action of sulphur compounds. With iron as a catalyst the results were more favorable, especially at pressures of several hundred atmospheres and at temperatures above 400° C. Teodorin's researches were carried out at the Königl. Technische Hochschule in Berlin and were published in 1912. This work was followed by that of Bergius² who studied the transformations of heavy mineral oils into low-boiling products by treatment with hydrogen without a catalyst, using a temperature of 400° C. and a pressure of about 100 atmospheres.

4802. Thereafter with numerous investigators entering the field, experimental work on the behavior of petroleum oils, heated under high pressure with and without hydrogen, expanded notably; various phases of hydrocarbon alteration which previously had received little or no attention at the hands of technologists becoming the subject of scrutiny. Snelling,³ for example, carried out tests on heating oils in an autoclave at a pressure of 600 to 800 lbs. per square inch. A process described in *Oildom* (December, 1914) called for pressures up to 1000 lbs. and the use of a catalyst of finely divided nickel.

¹ Studies on Rumanian Crude Oil Products, Dissertation, Berlin, 1912.

² *Z. angew. Chem.*, 1921, **34**, 341; *Brit. Chem. Abst.*, **1921**, 570A.

³ *Brit. Pat.* 18,419, Aug. 7, 1914; *Chem. Abst.*, **1916**, 388.

4802A. The oil vapors are passed through a chamber, containing a finely divided catalyst, such as asbestos, coated with nickel, on their way to the condenser. The heavy hydrocarbon is first purified from asphalt, sulphur, and other catalyst poisons, and is passed from the store-tank, together with hydrogen from a reservoir, along a pipe, where it mixes with nickel from a shot-flask device, entering the still through a rose. The still is fitted with an agitator. The distillation is effected at about 300° C. and under a pressure of 5–1000 lb. per sq. in. regulated by a weighted valve. The gases which escape from the condenser are burnt under the still, or, if rich in hydrogen, are readmitted to the still. The nickel is regenerated when necessary by washing it with benzol, calcining to oxide, converting into citrate or formate, and reducing with hydrogen at 320° to 350° C. Instead of providing the cracking-still with a large exposed upper surface, a reflux condenser may be used.

4802B. *Planes Limited* ⁴ produce saturated lighter hydrocarbons from heavier oil according to the following method:

The heavier oil together with nickel catalyzer and hydrogen or hydrogen-containing gas are run into a tall cracking-still, the latter being provided with a stirring device. As the temperature rises pressure is developed to the desired point when it is relieved by a weighted valve into an expansion chamber. This chamber is fitted with shelves on which are placed catalytic material. The vapors from the still pass through this chamber together with water gas and are saturated. They are then condensed. Oil, catalyser and hydrogen are continuously passed into the still until the residues are too heavy to be further cracked, when they are removed and the catalyser recovered. The waste gases may be returned to the still provided they are rich in hydrogen.

4803. Hydrogenation Contrasted with Treatment under Nitrogen Pressure.

The reality of the hydrogen function in berginization of mineral oils is brought out in Shatwell's work on Norfolk shale oil.⁵ The results of working in an atmosphere of hydrogen are contrasted with those obtained in nitrogen. The raw material had a density of 0.9850, was highly unsaturated (iodine value, Wijs, 882) and had a high sulphur content, 6.82 per cent. The final pressure fell with hydrogen, rose with nitrogen. The hydrogen product was much the lighter, sp. gr. = 0.9463; the nitrogen product (sp. gr. = 0.9712) was almost as dense as the original material. The immediate loss with hydrogen was 10 per cent, with nitrogen 14 per cent. The refining loss with hydrogen was 35.4 per cent on the gasoline, and 24.7 per cent on the kerosene. Of course all these figures for "losses" represent, in part at least, recoverable products such as hydrocarbon gases, phenols, acidic and basic substances. Hydrogenation greatly increased the yield of low-boiling fractions, i.e., from 6 per cent to 22.3 per cent for end-point 175° C. The sulphur content was reduced.

4804. Shatwell ⁶ reports analogous work on a gas-oil. Gas-oil having sp. gr. 0.8500, loss to sulphuric acid 10 per cent, iodine value 69.2, distillation range 230°–300°, was heated with hydrogen for six hours at 400°–415° (pressure 103–116 atmospheres), for four hours at about 400°–430° (pressure 110–142 atmospheres), with nitrogen for three hours at 386°–410° (pressure 116–155 atmospheres), and with hydrogen, first for one hour at 410° (pressure 107–108 atmospheres), and then, after cooling and replacing the gases by fresh hydrogen, for four hours at 403°–420° (pressure 118–130 atmospheres). The products were dark red, mobile liquids possessing the characteristic odor of cracked spirit, that obtained by heating with nitrogen being darkest in color and quite opaque. On distillation, the products yielded respectively, 44 per cent, 47 per cent, 38 per cent, and 48.8 per cent of gasoline fractions of boiling-point up to 175°, which on refining by successive agitation with sulphuric acid, alkali, and water, yielded colorless products. The refined gasoline from the hydrogenated products had a sweet odor, and retained its color after standing for sixteen months, that obtained from the oil heated with hydrogen in two stages being the best, but the gasoline from the oil heated

⁴ Brit. Pat. 5,245, Apr. 1, 1914.

⁵ *J. Inst. Petrol. Tech.*, 1925, **11**, 548.

⁶ *J. Inst. Petrol. Tech.*, 1924, **10**, 903; *Brit. Chem. Abst.*, 1925, 21B.

with nitrogen had a "cracked" odor and its color deteriorated on standing. In hydrogenating oils, hydrogen concentration appears to be a more important factor than the use of excessively high pressures.

4805. Mott and Dunstan heated gas-oil to 405°–420° for two and three-quarter hours under pressures to a maximum of 105–135 atmospheres, in the presence of hydrogen, nitrogen and steam respectively, the hydrogen and nitrogen being charged into the apparatus under a pressure of 22 atmospheres in the cold. The liquid product obtained when hydrogen was used, was superior in color and clearness, and in the absence of gumming constituents, to that obtained with nitrogen; on the other hand, analysis showed that the presence of hydrogen did not lead to hydrogenation of the liquid and did not even check dehydrogenation. About one-half of the hydrogen was fixed, but the hydrogenated products were gaseous.⁷

4805A. These results of Mott and Dunstan appear to be in contradiction with those of other workers. Shatwell,⁸ however, points out that the low final hydrogen pressure renders these experiments inconclusive.

4806. Gas-Oils Hydrogenated at Higher Pressures. Passager⁹ conducted experiments at pressures considerably higher than those used by Bergius. A gas-oil hydrogenated at 400° C. (752° F.) before treatment contained 34 per cent of constituents boiling at temperatures up to 300° C. (572° F.); after treatment such constituents formed 78 per cent of the oil. With a Pechelbronn crude oil residuum the percentage was raised from 22 to 42.3 per cent. When temperature and hydrogen content are kept constant, at temperatures of 400° to 470° C. (752°–878° F.), 200 atmospheres is the pressure at which the highest yield of easily liquefiable products is obtained. If pressure and temperature are kept constant, considerably higher yields of benzine-like derivatives are produced with the aid of hydrogenation than without. Fractions of ordinary gas-oil going over below 300° C., 16.8 per cent; with pressure and temperature kept constant, 39 per cent; pressure and temperature constant, with hydrogenation, 56 per cent.

4806A. Griffith¹⁰ has sought to correlate the value of gas-oils for gas making with their composition. The method was to measure the thermal value of the gases produced from cracking a given quantity of oil in a stream of hydrogen or nitrogen. A vertical silica tube into which the oil was dropped served as the furnace for the first experiments. When therms per gallon of oil were plotted against cc. of oil going through per minute, the curve rose abruptly to a maximum and then dropped off linearly. When packing sufficient to double the exposed surface was placed in the tube, the curve obtained was somewhat dissimilar, as if the products of surface reaction were not identical with those of gas reaction. The temperature of maximum efficiency in gasification was about 750°. Hydrogen raised the efficiency, as comparative runs with nitrogen showed. The hydrogen may react with gaseous or liquid hydrocarbons, it may retard the loss of hydrogen from the hydrocarbons, and it may react with the products of cracking while the temperature is still sufficiently high. The oils tested were analyzed; the highest thermal yields were from those containing the highest percentage of straight-chain compounds. Study of tar production required the use of a somewhat larger tube as furnace. As the rate of feeding was increased, the tar yields dropped to a minimum almost immediately and remained nearly constant. The "paraffin" content of the tar, that is, the percentage of substances not dissolved by sulphuric acid, was very high at low rates of feed. The pitch or residue after distillation of the tar to 360° increased with the rate of oil feed. Experiments with carbureted-water-gas sets, like those with the miniature apparatus, gave the maximum of therms produced per gallon of oil while the feed rate was still low.

⁷ *J. Inst. Petrol. Tech.*, 1924, 10, 911; *Brit. Chem. Abst.*, 1925, 121B.

⁸ *J.S.C.I.*, 1925, 44, 471.

⁹ *Erdöl u. Teer.*, Oct. 21, 1926, 669; *Univ. Oil Prod. Co. Bull.*, Nov. 20, 1926. Note para. 4690.

¹⁰ *J. Soc. Chem. Ind.*, 1929, 48, 252–63T; *Chem. Abst.*, 1929, 5565–6.

4807. Asphalt: Berginization. Bruylants,¹⁰ and Waterman and Kortlandt¹¹ have studied the berginization of asphalt. Bruylants, working in the Bergius laboratory at Mannheim, submitted crude Panuco asphalt, mixed with some ferric oxide, to a temperature of 420° C. and to a maximum hydrogen pressure of 137 atmospheres for one hour in a 5-liter rotating autoclave. The asphalt, originally thick, black and sticky with a density of 0.989, was converted into a mobile, fluorescent, reddish-brown liquid of density 0.866. There was a loss of 18 per cent, but not all of this was represented by permanent gases, some was material adhering to the walls of the autoclave. The increase in the hydrogen content of the liquid was negligible.

4808. Although a fall in pressure (17 atmospheres) occurred, most of the hydrogen was recovered in the residual gases: but *only about 25 per cent was uncombined*, the rest was chiefly in paraffin hydrocarbons. The original material had contained 12.4 per cent boiling below 300° C. The product gave 58 per cent boiling below 300° C. and 28 per cent below 150° C., all by weight. Another, heavier asphalt (Pechelbronn) gave similar results, though it required a temperature of 455° C.

4809. In neither case was there any coke formation, a result which is characteristic of successful berginization and which contrasts favorably with that of the best cracking processes when applied to such materials.

4810. Smolenski and Badzynski¹² find that petroleum asphalt heated at 400° for twelve hours with hydrogen at above 100 atmospheres yields 60 per cent by weight of liquid hydrocarbons, similar to those obtained by the distillation of Galician light petroleum, and of which 32 per cent boils below 150° and 36.5 per cent from 150° to 300°. The solid residue (25–30 per cent) contains 87 per cent carbon and 4 per cent hydrogen, and is a good substitute for coke. About 15 per cent of the original weight of asphalt is evolved as gaseous products containing about 40 per cent methane and 40 per cent hydrogen. Somewhat lower yields of liquid hydrocarbons are obtained by the substitution of water-gas for hydrogen.¹³

4811. Waterman and Perquin¹⁴ conclude that in berginization of petroleum the main feature is not the saturation of preformed unsaturated hydrocarbons but the suppression of polymerization and of formation of coke. This, in the author's opinion, is a feature which clearly differentiates the process from cracking methods. Pyrolytic cracking, as has already been pointed out, is characterized by polymerization and coke formation. Elimination of these undesirable changes should relieve the oil refinery of one of its most difficult problems.

4812. In the adaptation of a berginization plant to the treatment of liquids, specifically of petroleum hydrocarbons, the chief modification is obvious, viz., that due to the great ease with which a liquid may be injected into the reaction chamber. Furthermore, since in berginization there is no coking, there is no solid residue to remove.

¹⁰ *Bull. Soc. Chim. Belg.*, 1923, **32**, 194.

¹¹ *Rec. Trav. Chim. Pays-Bas*, 1924, **45**, 249.

¹² *Przemysł Chem.*, 1928, **12**, 117.

¹³ *Brit. Chem. Abst.*, 1928, 661B.

¹⁴ Hydrogenation in the petroleum industry, *J. Inst. Petr. Tech.*, 1925, **11**, No. 28.

4813. Berginization of Heavy Hydrocarbon Oils. Bergius¹⁵ heats heavy hydrocarbon oils to 400° C. with hydrogen under 100 atmospheres pressure for the production of light oils. Water-gas or other hydrogen-carbon monoxide mixture may be used. Mention is made of the addition of metals, metallic oxides and hydroxides as desulphurizing agents and as hydrogenation catalysts. Figures are given for a run on a Galician gas-oil of b.p. 270°–360° which gave a 97 per cent yield, 45 per cent boiling below 180° C. Eleven kilos of gas tar are heated with hydrogen at 100 atmospheres pressure, to 400° C. After four hours the mass is distilled at about 250° C., and about 60 per cent of distillate resembling petroleum oil is obtained, which can be further treated by rectification.¹⁶

4814. Hydrogenating Oils, Asphalt and Similar Materials.¹⁷ The hydrogenation of carbonaceous solids in the presence of combined sulphur¹⁸ is applied also to the treatment of rock oils, shale oils, resins, ozokerite, asphalt and the like, or fractions, residues or acid sludge or conversion products of these materials. An excess of hydrogen or other reducing gas is preferably used under pressure; e.g., residues of American petroleum are treated with hydrogen under 200 atmospheres pressure at 450°–500° C. in the presence of precipitated cobalt sulphide and the issuing gases are cooled to condense the light oil produced.¹⁹

Great credit should be given the I. G. Farbenind. A.-G. for the development of hydrogenolysis catalysts which are immune to sulphur, that is, retain adequate activity in the presence of the sulphur compounds of petroleum oils. By the employment of such sulphur-active, or *sulphactive* catalysts the scope of hydrogenolysis of mineral oils has been greatly expanded and the commercial possibilities correspondingly widened.

4815. Hydrogenation of Hydrocarbons.²⁰ The volatile matter of a hydrocarbon substance is vaporized and mixed with hydrogen under pressure.²¹

4816. Desulphurizing Preparatory to Hydrogenation.²² Mineral and tar oils (coal is also mentioned) with water or steam, *with or without* hydrogen are treated at 200 atmospheres pressure and 500° to 550° C. in the presence of a contact mass containing iron and manganese; the sulphur is removed and condensed as a solution of hydrogen sulphide. (The oil is then passed, at the same temperature and pressure, over a catalyst containing molybdenum.)

4817. Alkali Metal as Desulphurizer.²³ In berginization of mineral oils, etc., the addition of 5 per cent of alkali metal is made for removal of sulphur and to assist in the conversion. Other additions may be porous substances, fuller's earth, charcoal, and coke ash.²⁴

4817A. Hydrogenating and Purifying Mineral Oils.^{24a} Mineral oils, crude naphthalene, oils from coal, etc., are subjected to the combined action of hydrogen and sodium under pressure and at a temperature of at least 300°.

¹⁵ U. S. Pat. 1,344,671, June 29, 1920; *Chem. Abst.*, 1920, 2550.

¹⁶ Cf. Austr. Pat. 71,208, June 26, 1916; French Pat. 470,551, Apr. 6, 1914; *J.S.C.I.*, 1915, 167; Brit. Pat. 5,021, Mar. 31, 1915; addition to 18,232 of 1914; *J.S.C.I.*, 1916, 732; Brit. Pat. 4574, 1914; Ger. Pat. 304,348, 1913.

¹⁷ Brit. Pat. 249,493, Mar. 19, 1925, to I. G. Farbenind. A.-G.

¹⁸ Described in Brit. Pat. 247,584; *Chem. Abst.*, 1927, 21, 643.

¹⁹ Brit. Pat. 249,501 specifies a similar process except that catalysts containing molybdenum or its compounds are used as described in Brit. Pat. 247,583 (*Chem. Abst.*, 1927, 21, 643) and Brit. Pat. 247,586 (*Chem. Abst.*, 1927, 21, 643); *Chem. Abst.*, 1927, 21, 1005.

²⁰ Can. Pat. 223,195, Aug. 29, 1922, to Benson.

²¹ *Chem. Abst.*, 1922, 16, 3903.

²² Brit. Pat. 257,912, Sept. 2, 1925, to I. G. Farbenind. A.-G.

²³ Dutch Pat. 13,594, Oct. 15, 1925, to the Internationale-Bergin Compagnie voor Olieen Kolen-Chemie.

²⁴ *Chem. Abst.*, 1926, 20, 495; Brit. Pat. 213,661, Jan. 2, 1923, to same patentee. French Pat. 632,509, July 7, 1926 (addition to 559,787), to the same patentee, adds the preliminary step of treating the raw material with solid potassium hydroxide, or with metallic oxides, at a high temperature under high hydrogen pressure.

^{24a} Hofmann (to Internationale Bergin-Compagnie voor Olieen Kolen-Chemie), U. S. Pat. 1,729,943, Oct. 1, 1929; *Chem. Abst.*, 1929, 5568.

4818. In order to obtain a high yield of low-boiling hydrocarbons hydrogen is circulated in a closed circuit in such excess that the partial pressure of the desired product is less than 10 per cent of the total pressure. Crude mineral oil can be cracked to obtain 60 per cent of motor spirit by atomizing it with heated hydrogen in an aluminum-lined vessel and passing it at 475° C. and 200 atmospheres pressure over molybdenum and chromium oxides.²⁵

4819. In the hydrogenation of mineral oils the deposition of carbon on the heating surfaces is avoided by effecting the heating in contact with moving surfaces such as nickel-chromium, cobalt-nickel, molybdenum, iron, chromium, manganese, tungsten, vanadium, tantalum, copper or noble metals or their alloys or silicides.²⁶

4820. Hydrocarbon vapors with water-gas, methane, etc., pass through a narrow high temperature zone where they are exposed to a flat flame. Among the metals used to prevent separation of carbon are cobalt, chromium, manganese, molybdenum, nickel and tungsten.²⁷

4821. Crude oil is forced through a vertical high-pressure reaction chamber lined with aluminum, in which the oil in a thin layer comes in contact with excess of hydrogen at 450°–475° C. and under 200 atmospheres pressure in the presence of molybdenum or magnesium oxide supported on an inert carrier.²⁸

4821A. Klever^{28a} outlines a method of treating tar oils at a high temperature and under high hydrogen pressure in the presence of aluminum, copper, silver, zinc, cadmium, magnesium, alkaline and alkaline earth metals and their compounds to produce lubricating oils.

4822. Bergius²⁹ describes a process of hydrogenating and decomposing hydrocarbons which is chiefly concerned with recovery of hydrogen from the lightest fraction produced. Hydrogen and hydrocarbon vapors having been caused to interact in a reaction vessel the issuing gases and vapors are passed through a condenser, then through wash-oil, all without lowering the pressure. The residual hydrogen-containing gases return to the reaction chambers. Hydrocarbon gases which have been absorbed by the wash-oil are separated, heated to a high temperature to decompose them into hydrogen and carbon and the hydrogen so produced is used in the reaction vessel.³⁰

4823. Not unlike this is the process³¹ described below. Oils containing unsaturated hydrocarbons are heated in a still and the vapors mixed with hydrogen. The mixture is compressed to a pressure of 4–5 atmospheres and passed through a condenser. The condensed hydrogenated products are collected and the uncondensed gas is treated for the production of hydrogen. The gases may be passed over a catalyst between the compressor and the outlet of the condenser.³²

4824. Nitrogen Compounds as Catalysts. The methods described in paragraphs 4515–4518 are extended to the treatment of bitumens, their components or derivatives, such as crude oil, oil distillates, ozokerite, mineral pitch, cracked oils and acid sludge. Silicon nitride or titanium nitride may be used as catalysts with hydrogen alone, or mixtures of hydrogen with nitrogen and traces of ammonia may be passed together with the material to be hydrogenated over a heated catalyst such as an iron contact mass activated as for the ammonia synthesis.³³

²⁵ Brit. Pat. 272,556, June 14, 1926, by the I. G.; *Chem. Age* (London), 1927, **17**, 173.

²⁶ *Chem. Abst.*, 1928, **22**, 1847; Brit. Pat. 272,483, June 11, 1926, to I. G. Farbenind. A.-G.

²⁷ Brit. Pat. 264,845.

²⁸ Brit. Pat. 272,190.

^{28a} German Pat. 301,773, June 10, 1916.

²⁹ U. S. Pat. 1,607,939, Nov. 23, 1926.

³⁰ *Chem. Abst.*, 1927, **21**, 318.

³¹ Brit. Pat. 174,106, Aug. 12, 1920, to Stephens.

³² *Brit. Chem. Abst.*, 1922, **41**, 168A.

³³ Brit. Pat. 250,582, Apr. 15, 1925; 251,264, Apr. 25, 1925, to I. G.; *Chem. Abst.*, 1927, **21**, 1349.

4825. In the conduct of hydrogenation at elevated temperatures, intimate contact between the materials and the hydrogenating gases is obtained by passing them into contact with the materials through a porous mass such as a septum of sintered glass powder, quartz, earthenware, metals or charcoal. The interior of the reaction vessel may be lined with an alloy of chromium 10, molybdenum 2, cobalt 10 and iron 75 parts.²⁴

4826. Catalyst Dust Suspended in Vapor Phase.²⁵ One process involves the circulation in the reaction space of catalyst dust by means of an inert or of a reactant gas. The method is said to be particularly applicable to destructive distillation hydrogenations, to the methanol and the ammonia synthesis and to other reactions under high pressure. An example is given in which a mixture of hydrogen and heavy oil vapor passes through a porous fireproof plate carrying a molybdenum-chromium catalyst in the form of dust. The catalyst is whirled in the reaction space by the gases, and the reaction is effected at 460° C. and 20 atmospheres pressure. The catalyst is subsequently removed by baffles or a wire screen.²⁶

4827. Distillation, Cracking, and Hydrogenation of Oils and Tars.²⁷ The raw material is atomized by being fed on to a series of rapidly rotating discs, and is simultaneously heated by circulating hot gases and vapors through the apparatus. The issuing gases and vapors are passed through a superheater and recirculated through the atomizer, part being withdrawn periodically and passed to a condensing system. The process may be carried out in the presence of a hydrogenating gas, and, if necessary, under pressure.

4828. Berginization of Squalene and *d*-Pinene.²⁸ Squalene is a hydrocarbon oil present in large quantities in the liver of certain sharks. The interest of this work is in connection with speculation as to the origin of petroleum. Samples of squalene having d^{20}_D 0.8559 and ignition temperature (Moore) 259° were berginized in a small bomb. The resultant liquid had d^{20}_D 0.8256, and yielded on distillation 57 per cent of spirit up to 200°, 23 per cent of kerosene at 200°–300°, and residual heavy oil. The spirit fraction contained 10 per cent of unsaturated, 26 per cent of aromatic compounds, 24 per cent of open- and 40 per cent of closed-chain paraffins. In a further berginization test at 470° for one hour with initial pressure of hydrogen of 80 atmospheres, falling to 63 atmospheres on cooling, the liquid yield was 75 per cent, the absorption of hydrogen 3.45 per cent, and the product had d^{20}_D 0.8129 and yielded 59.3 per cent of spirit up to 180° and 28.2 per cent of kerosene up to 300°, no wax being found in the residue. It contained 6.8 per cent of unsaturated and 17.9 per cent of aromatic compounds and 75.3 per cent of paraffins. The presence of isopentane was well marked. A sample of *d*-pinene when berginized gave very similar results to squalene, as was the case with some lignite oils, but the latter yield some 20 per cent of phenols. The higher phenols when berginized are converted into paraffins and lower phenols; the lower the phenol the more soluble it is in water.²⁹

4829. A proposal³⁰ to hydrogenate petroleum and its residues in a continuous manner, in a liquid state, was made by Ellis,³⁰ who has advocated the treatment of petroleum, pitches, tars, asphaltic oils and malthas with hydrogen.

4830. Hydrogenation of Refinery Distillates. In a country as rich as the United States in supplies of petroleum, at first sight there would scarcely seem a need for hydrogenation processes which to other nations not so fortunately supplied with oils from natural sources, represent a vital necessity. It is easy to understand why Germany, for example, should be deeply interested in the hydrogenation of lignite coal, and the like, to produce liquid fuels. In the handling of petroleum oils, however, especially in cracking operations, there are produced enormous quantities of residues of comparatively low value, together with a surfeit of coke or carbon. In the neighborhood of some of our large oil refineries

²⁴ *Chem. Abstr.*, 1928, **22**, 1847; *Brit. Pat.* 272,539, June 11, 1926, to I. G. Farbenind. A.-G.

²⁵ *Brit. Pat.* 274,904, July 24, 1926, to the I. G. Cf. paras. 4701, 4702, 4714 and 5035.

²⁶ *Chem. Age* (London), 1927, **17**, 311.

²⁷ *Kohlenveredlung A.-G.*, *Brit. Pat.* 293,430, July 6, 1928; *Brit. Chem. Abstr.*, **1929**, 1041B.

²⁸ Ormandy, Craven, Heibron and Channon, *J. Inst. Petrol. Tech.*, 1927, **13**, 1.

²⁹ *Brit. Chem. Abstr.*, 1927, 692B. See para. 3000.

³⁰ *U. S. Pat.* 1,345,589, July 6, 1920.

not infrequently one will find areas heaped high with waste carbon removed from cracking stills. Losses by cracking through formation of fixed gases and production of coke are considerable and hydrogenation has come forward to provide the means of conversion of crude oil in its entirety into serviceable fractions of good quality available as motor fuels, kerosene, lubricants and other purposes where relatively high-grade products are required. We have elsewhere considered the hydrogenation of mixtures of petroleum oil and powdered coal. Hydrogenation of these mixtures can be carried out almost as simply as the treatment of the oil itself by hydrogen with the added advantage that from a relatively cheap raw material—coal—there is obtained a substantial yield of volatile motor fuel. While powdered coal itself offers many difficulties in treating in a continuous manner under approved conditions of hydrogenation, a mixture of ground coal and oil can be handled in a manner similar to the oil itself, that is, pumped, heated and otherwise treated as a liquid. If refinery residues of a liquid character can be mixed with bituminous coal and hydrogenated to convert both oil and solid components very largely to useful liquid products, eventually there should result a considerable advantage to the refinery and what, perhaps, is even more important, another step towards the conservation of our natural resources in liquid fuels. In this connection Haslam and Ward⁴¹ several years ago referred to hydrogenation in the following terms: "its application in the United States as a means for caring for any petroleum shortage apparently awaits only proper economic incentive."

4831. That incentive has at length arisen, bringing to the petroleum oil industry wholly revolutionary methods of oil conversion and refining. In this country the pioneer in petroleum hydrogenolysis is the Standard Oil Company (New Jersey.) Starting with test units of about one barrel daily capacity, the utility and flexibility of refining by hydrogen (hydroforming and hydrofining) was established. A pilot plant of one hundred barrels daily capacity then was built and after its successful operation was assured the construction of several units of five thousand barrels daily capacity was undertaken.⁴²

⁴¹ *Mech. Eng.*, 1928, 50 26.

⁴² *Ind. Eng. Chem.* (News Edition), July 10, 1929, 3. Note Howard's process, para. 4619. The Standard Oil Company (New Jersey) has entered into an agreement with the German I. G. Farbenindustrie, whereby a jointly owned corporation (Standard-I. G. Company) has arranged to acquire the patents of both parties in connection with the commercial development of the hydrogenation of coal and oil for operation in all countries outside of Germany. The significance of the new contract as applied to the United States is that the hydrogenation process will be adapted commercially in this country to make gasoline and other products under the guidance of American oil interests with the full cooperation of the developers of the process. *Ind. & Eng. Chem.*, 1930, 22, 5. A further expansion of the plan of development of hydrogenation of petroleum in this country has resulted in the formation of the Hydro Patents Company under which a large proportion of the refiners of the United States are licensed. Note also *Chem. & Met. Eng.*, 1929, 678 and 761; 1930, 153; Howard, *Manufacturers' Record*, Jan. 13, 1930, 57. Howard states that two of the main things which hydrogenation is expected to accomplish are: (1) Make possible the manufacture of a barrel of gasoline out of a barrel of crude. In other words, to increase the proportion of lighter products obtained from crude oil as needed; (2) In this way to reduce the load on crude production, lessen the present over-supply of heavy fuel oils and gradually achieve an equilibrium between supply and demand. Hydrogenation process to be used first in conversion of heavy fuel oil,

4832. From an inspection of the chapters discussing the subject of petroleum hydrogenolysis, it will be observed that a new technology of petroleum is coming into being, a technology which is destined to modify profoundly the course of development of the industry during the next decade, a technology so divergent from the practice of the present oil refinery that mastery of the ramifications of hydrogenolysis will exact from the oil technician a high measure of study and specialization. Hydrogen, an element usually regarded as having only moderate reactive qualities, has now become a singularly potent medium of attack on petroleum under the new methods of application. Its power of seeking out what may be termed "atomic impurities" (sulphur, oxygen, nitrogen, and the like) in liquid petroleum and converting these impurities into gases which are readily removed from the field of reaction, seems scarcely less than magical. Known refining methods other than *hydrogenolysis* unfortunately result in the removal of the actual compounds or molecules in which the atomic impurities are found in the combined state. By such treatment these compounds are lost because they are eliminated in the refining wastage and yields, therefore, are correspondingly reduced.

4833. Hydrogenolysis, on the other hand, seems to involve the plucking out of the atomic impurities without necessarily removing and destroying the entire molecule harboring the impurities. A molecular structure remains which may be expected to be quickly repaired normally by union with hydrogen or as a result of its presence. Thus a *hydrocarbon* offers itself in place of the former impurity-carrying compound, whether this be mercaptan, carboxylic acid, nitrogen body, or whichever compound may have been subjected to the selective atomic stripping accompanying hydrogenolysis. Refining losses thereby are minimized or disappear. Volumetric yields of over 100 per cent frequently result. The oil has thus been *hydrocarbonized*. The term "hydrocarbonize" is used not in the sense of conveyance of extraneous hydrocarbons to the oil to unite therewith, but as an indication of the transformation of non-hydrocarbon bodies to strict hydrocarbon entities.

4834. In general the process employed by the Standard Oil Company (New Jersey) consists in bringing together crude, residues or distillates and hydrogen under high pressure, in the presence of a sulphactive catalyst, at temperatures usually ranging from 600° F. to about 1000° F., and separating from the hydrogenated product any excess hydrogen, which excess is recycled through the system. The hydrogen may be made either from natural gas, refinery gas, or coal—whichever happens to be the cheapest for a given locality.

4835. The cost of operation probably will vary somewhat, the exact figure being dependent on the particular variation of the process being used, the charging stock, the cost of hydrogen, fuel, steam, power, and labor.

Truesdell, *Natl. Petroleum News*, 1929, **21**, No. 28, 27-9; *Chem. Abst.*, **1929**, 4561. Comments on the I. G. Standard Oil process at a meeting of the Koninklijke Petroleum Mij, *Frankf. Zeitung*, June 28, 1928, No. 474; *J. Soc. Chem. Ind.*, Aug. 9, 1929, **48**, 791; Cf. Florian, *Petrol Times*, Aug. 31, 1929, 391. Patent rights on hydrogenation, of the Standard-I. G. Co., transferred to the Hydro Patents Co., *Ind. Eng. Chem.*, News Edit., July 20, 1930, 6. Petroleum becomes a chemical, Howard, *Chem. Markets*, July 30, 1930, 43. Eighty-five per cent gasoline yield by I. G. hydrogenation, Foster, *Natl. Petroleum News*, 1930, **22**, No. 33, 27-31.

× Two features of outstanding importance are: (1) The relative independence of quality of product from the character of the crude material; and (2) the flexibility of the process and plant, since widely varying hydrogenolytic operations may be carried out without material changes in plant construction. A few of these hydrogenolyses are noted below.

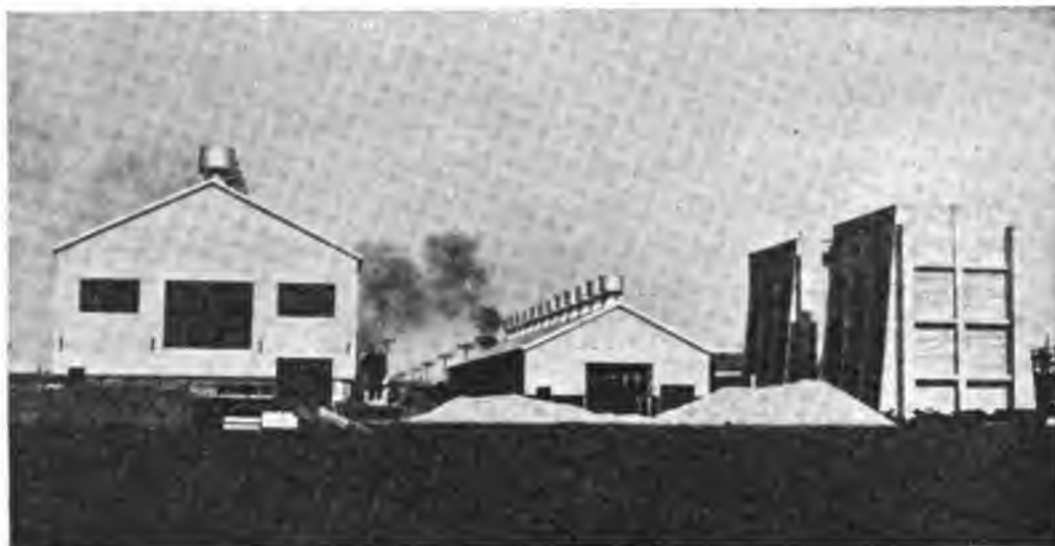


FIG. 109.—PETROLEUM HYDROGENATION PLANT.

Gas compressor house on left, oil pump house in center, and reinforced concrete stalls containing reactors and heat exchangers on right. (Plant in construction.)

4836. Hydrogenolysis of Fuel Oil to Gas-Oil and Gasoline. Residues from crude stills or cracking coils may be hydrogenolyzed to produce in excess of 100 per cent yield of a product consisting of gas-oil and gasoline, the percentage of gasoline ranging from 5 per cent to 35 per cent, depending upon conditions, the balance being a distillate product. During hydrogenolysis, the asphalt is completely converted (hydrobleached) and two-thirds to three-fourths of all the sulphur in the stock charged eliminated. This sulphur comes out as hydrogen sulphide and is scrubbed out of the recycle gases. Even if the product charged is highly asphaltic and of high sulphur content, the gasoline produced is easily finished to give a low-sulphur, gum-stable product—usually by caustic wash only. The anti-knock value of the gasoline is dependent somewhat on conditions, particularly the type of charging stock—crude residues from Smackover, Venezuela, Colombia and similar crudes giving lower knock-rating gasolines than residues from Mid-Continent crude. The gas-oil, in addition to having a relatively low sulphur content, may be cracked subsequently to give a gasoline which finishes to specification easily, even though the gas-oil was produced by hydrogenolyzing a high-sulphur, high-asphalt crude or residue. The workability of this phase of process has been demonstrated on fuel oil residues from reduced Crane Upton, Panuco, Venezuelan, Panhandle, Mid-Continent, Talang Akar, Long Beach, Alamitos, Smackover, Reagan, and other crudes.

4837. One of the applications of this phase of hydrogenolysis will be to run these heavy asphaltic products to 25 or 30 per cent of gasoline and the balance gas-oil. The gas-oil then will be cracked to produce gasoline; so much of the cracking coil tar as is needed for the production of steam and power in the refinery will be used as fuel; and the balance of the tar will be recycled back to the hydrogenolysis unit. In this way the maximum gasoline yield will be obtained with the minimum hydrogen consumption. Depending upon the stock and operating conditions, a yield of 80 to 90 per cent of gasoline may be obtained by this method. If none of the tar were burned for fuel oil, the yield would be approximately 100 per cent. The methods described are those which have been worked out by the Standard Oil Development Company in collaboration with the I. G. Company.

4838. The following table gives an "inspection" of topped Crane Upton crude oil:

A. P. I. gravity.....	23.0°
Per cent at 400° F.....	1.5
Per cent at 460° F.....	7.0
Per cent at 650° F.....	46.5
Per cent at 700° F.....	72.0
Per cent sulphur.....	1.51

This stock was hydrogenolyzed to yield the following product:

A. P. I. gravity.....	35.1°
Sulphur, per cent.....	0.48
Per cent off at 374° F.....	21.0
Per cent off at 400° F.....	25.5
Per cent off at 460° F.....	36.0
Per cent off at 650° F.....	77.5
Per cent off at 700° F.....	85.5

The above "inspection" is on the liquid product and does not include a small portion of absorption naphtha produced concurrently. The 400° end point gasoline produced amounted to 26.3 per cent on the feed and had a sulphur content of 0.056 per cent.

4839. In hydrogenolyzing a 7.2 A. P. I. gravity Tube-and-Tank tar containing 2.77 per cent sulphur, the hydrogenolyzed product gave the following "inspection":

Sulphur, per cent.....	0.49
Per cent at 374° F.....	18.0
Per cent at 460° F.....	32.0
Per cent at 650° F.....	73.5

The gasoline from this hydrogenolyzed product had a sulphur content of 0.071 per cent.

4840. Conversion of Gas-Oil to High-Grade Burning Oils. Light gas-oils may be hydrogenolyzed to produce water-white distillates and burning oils of high quality. In general, these products meet specifications as to sulphur, color, and smoke tendency with no other treatment except reduction to flash. The product consists of approximately 15 to 20 per cent gasoline, the balance being high-grade kerosene or "water white." In view of the fact that hydroforming takes a charging stock of higher viscosity than the final product desired, large yields of burning oils can be produced by this means. High quality burning oils have been made from the following stocks: Light Mid-Continent gas-oil; naphtha bottoms containing a little Smackover gas-oil; light Colombia refined oil distillate; Alamitos (California) heavy refined oil distillate; Long Beach

refined oil distillate; reduced cracking coil distillate from Tube-and-Tank cracking; and West Texas gas-oil. The following illustrations show the possibilities of this phase of the process:

4841. One hundred volumes of first rerun from Mid-Continent having the following characteristics:

A. P. I. gravity.....	40.6°
Refined oil viscosity.....	430 sec.
Sulphur.....	0.26 per cent
Color.....	light brown

was hydrogenolyzed to give about 102 volumes of the following product:

A. P. I. gravity.....	47.2°
Viscosity.....	320 sec.
Sulphur.....	0.011 per cent
Color.....	+25
Flash.....	below 60° F.

This product gave, on topping for flash, 10 volumes of gasoline and 92 volumes of the following product:

A. P. I. gravity.....	44.8°
Refined oil viscosity.....	385 sec.
Sulphur.....	0.01 per cent
Color.....	+25
Abel flash.....	105° F.
Doctor test.....	pass
Corrosion.....	pass

4842. One hundred volumes of Alamitos (California) light gas-oil produced 102 volumes of hydrogenolyzed stock, which, on reducing to flash, gave 29 volumes of gasoline and 73 volumes of export refined oil. The export refined oil gave the following inspection:

A. P. I. gravity.....	42.8°
Refined oil viscosity.....	420 sec.
Sulphur.....	0.037 per cent

This refined oil amounted to 19.5 per cent on the crude.

4843. From gas-oil having the following inspection:

A. P. I. gravity.....	35.3°
Refined oil viscosity.....	705 sec.
Sulphur.....	0.761 per cent,

export water white was made of the following quality, with a yield of 75 per cent on the charging stock:

A. P. I. gravity.....	44.7°
Refined oil viscosity.....	407 sec.
Sulphur.....	0.015 per cent

4844. Combination Fuel Oil and Refined Oil Hydrogenolysis. The following is given to show a possible combination of the fuel oil and refined oil modifications:

One hundred volumes of 27.6 Alamitos (California) crude having a sulphur content of 0.797 per cent, gives on straight distillation the following products:

- (a) 18 gals. of gasoline (gravity 52.5; sulphur 0.026 per cent).
- (b) 30 gals. of gas-oil (gravity 36.4; sulphur 0.55 per cent).
- (c) 52 gals. of fuel oil bottoms (gravity 14.7; sulphur 1.14 per cent).

4845. Hydrogenolyzing the gas-oil to "water white," and the fuel oil to gas-oil and gasoline, and admixing the gasoline produced in each of the hydrogenolyses with the straight-run gasoline gives the following yields:

(a) 42 gals. gasoline (gravity 54.1; sulphur 0.042 per cent).

(b) 20 gals. export refined oil (gravity 42.8; sulphur 0.037 per cent; R. O. viscosity 420).

(c) 39 gals. gas-oil (gravity 25.7; sulphur 0.33 per cent).

✦ **4846. Lubricant Hydrofining.** Special high-pressure treatment of lubricating fractions of petroleum oils with compressed hydrogen, usually in the presence of sulphactive catalysts, provides a means of obtaining almost unlimited supplies

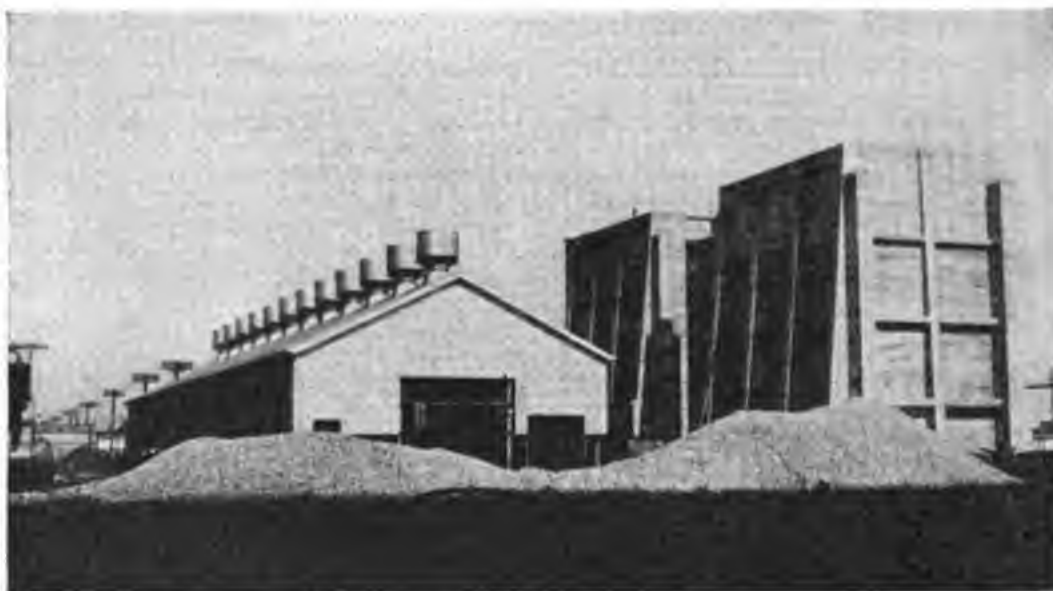


FIG. 110.—PORTION OF PETROLEUM HYDROGENATION PLANT. (In construction.)

of high-grade lubricating oils from relatively low-grade stocks. Other things being equal, a lubricating oil may be rated on its change in viscosity with the temperature. The less this change, that is, the less the thinning of the oil which occurs as the temperature rises, the more highly the oil will be regarded for its lubricating properties. To lubricate a machine, for example an internal combustion engine, to best advantage the oil should be thin enough, when the motor is started in the cold, to prevent impairment of the moving parts. As the motor becomes hot through operation the oil will grow thinner and its lubricating qualities may be expected to diminish. Therefore, oils which alter to only relatively small degree with change in temperature under operating conditions are particularly desired.

Viscosity is recognized by the refiner and oil user as the most important single characteristic of a lubricating oil, but its significance is complicated by the fact that the temperature-coefficient of viscosity varies widely with different

types of oil. Dean and Davis^{42a} have provided a unit known as the *viscosity index*, which expresses with adequate quantitative accuracy the changes taking place in the viscosity of an oil with alteration in the temperature.

4847. In general, oils of the paraffin base type exhibit a lesser change in viscosity than other available grades, that is, they have a relatively high viscosity index. With the rapidly growing demand for high-grade lubricants for automobile and airplane purposes hydrogenation has come forward to make us entirely independent of paraffin base oils. This finding is of great importance because the supply of paraffin base oils is comparatively limited. By the hydrogenation treatment oils which previously thinned or lost body rapidly with advance in temperature are found to acquire a notable viscosity stability or resistance to viscosity change with temperature. Oils from various sources, irrespective of their specific chemical composition, may be improved with respect to viscosity index to such a degree that no longer will the paraffin base oils represent a particular high quality of lubricant. Their significance in this respect is destined to be lost. In fact, special hydrofining enables oils of other types to acquire a viscosity index exceeding that of paraffin base oils. Superparaffins may be said to result.

4848. All lubricating oils used in internal combustion engines form carbon deposits during operation. These vary in character, ranging from flocculent and easily dislodged carbon to hard and adherent material. Some of the paraffin base oils are the worst offenders with respect to the formation of adherent carbon. Were it possible to find in abundance an oil which (1) changes only to a small degree in viscosity with the temperature and (2) yields only flocculent carbon, an important commercial requirement would be met. The hydrogenation process apparently has solved the problem of producing such an oil. By hydrofining oils of the flocculent carbon type having initially a low viscosity index, the latter is raised adequately so that the equivalent of a paraffin base oil possessing the valuable property of carbon-detachability results. Thus a new species of lubricating oil is obtainable, namely, one having a high viscosity index coupled with the detachable-carbon quality; the characteristics of the paraffin base oil without its defects.

4849. Treatment with hydrogen causes a virtual improvement in flash point. The property of high flash point seems to be reflected in some measure in reduced consumption of the oil by an internal combustion engine. Apparently there exists a relationship between flash point and rate of engine consumption of oil which tends to render the hydrogenation process one of particular value from this standpoint. Moreover, there is a reduction in carbon (Conradson test) and in gum formation. The hydrofined lubricating oils are not as readily oxidized as the untreated oils, hence do not sludge easily. Hydrogenolysis also brings about an improvement in color.

4850. Furthermore the treatment results in a notable reduction in sulphur: the oil is *hydrunsulphed*. In fact that tendency of hydrofining to replace by

^{42a} Dean and Davis, Standard Oil Development Company, Bayonne, N. J., *Chem. Met. Eng.*, Oct., 1929, **36**, No. 10.

hydrogen the atoms of sulphur, oxygen and nitrogen as they occur in compounds present in the oil (or perhaps partly to eliminate them in some other manner) is truly described by the term *hydrocarbonizing*. Probably the term *hydrofining* is best applied to those treatments by hydrogen which are carried out at temperatures in the lower ranges, including simply hydrunsulphing and hydrocarbonizing, where no extensive alteration of the carbon-containing molecule occurs. On the other hand, where great disturbance of carbon structure results the process is better denominated *hydroforming*. Thus the conversion of low-grade lubricating oils to those of high quality usually is a hydroforming process, the stock thereby being *hydrolubriformed* to yield a *hycosol* or *hydrocosol*. If the



FIG. 111.—REINFORCED CONCRETE STALLS CONTAINING PETROLEUM REACTORS AND HEAT EXCHANGERS.

same stock is subjected to a milder treatment involving no substantial change in the carbon structure, only a limited formation of lighter products, no material change in the viscosity-temperature curve and practically no reduction of Conradson carbon, the operation is termed *hydrolubrifining*, yielding a hydrolubrifined oil. The subjection of smoky kerosene stocks to hydroforming action yields *hydroluminized* or *hydroluminized* kerosenes of greatly improved burning properties. Frequently two or more reaction types or phases progress simultaneously, such as hydrunsulphing during hydroforming, or hydrocarbonizing when hydroluminizing. Likewise the conversion of dark-colored petroleum residues or distillates into light-yellow to water-white liquids, an action referred to previously as hydrobleaching, may progress concurrently.

4851. Conversion of Low-Grade Lubricating Distillates to Higher-Grade Lubricating Oils. By charging a low-grade lubricating oil distillate, a high-grade semi-finished lubricating oil may be produced. The hydrogenolysis is conducted to raise the gravity, increase the flash, lower the change in viscosity with temperature, and decrease the Conradson carbon. Naphthenic acids and asphalt present in the lubricating distillate are eliminated. An oil of good demulsibility is obtained. Mid-Continent lubricating oils have been hydrogenolyzed to give products of the best paraffin base quality. Distillates from Venezuela, Colombia, and West Texas crudes have given lubricating oils equal to high-grade Mid-Continent and Ranger Burbank or, by taking a lower yield, an oil corresponding in quality to a high-grade paraffin base type results. In general, in hydrogenolyzing lubricating oil distillates, the product on a volume basis amounts to somewhat more than the stock charged. Yields given below are based on the product, and not the charge, and therefore all yields on the stock charged are possibly 2 to 5 per cent higher.

4852. For the purpose of making a heavy motor oil of good paraffin base quality, there was hydrogenolyzed a Mid-Continent "Bright Stock" of the following specification:

A. P. I. gravity.....	23.0°
Viscosity at 100° F.....	2940 sec.
Viscosity at 210° F.....	149 sec.
Conradson carbon.....	2.86
Flash.....	510° F.

On reducing the hydrogenolate to viscosity, a yield of 80 per cent of the following product was obtained:

A. P. I. gravity.....	28.3°
Viscosity at 100° F.....	671 sec.
Viscosity at 210° F.....	74 sec.
Conradson carbon.....	0.32
Flash.....	480° F.

The balance, 20 per cent, consisted of gasoline, gas-oil and spindle oil.

4853. To produce a Mid-Continent quality, 280 viscosity at 100° F. oil, a Colombia lubricating distillate having the following "inspection" was hydrogenolyzed:

Gravity A. P. I.....	22.1°
Viscosity at 100° F.....	613 sec.
Viscosity at 210° F.....	60 sec.
Flash.....	420° F.
Conradson carbon.....	0.195

The hydrogenolate on distillation gave:

8 gals of gasoline,
29.5 gals. of 30° gravity gas-oil,
62.5 gals. of lubricating oil equal to that from Mid-Continent of the following "inspection":

Gravity A. P. I.....	27.1°
Viscosity at 100° F.....	286 sec.
Viscosity at 210° F.....	50 sec.
Flash.....	410° F.
Conradson carbon.....	0.01
Color.....	10 Robinson

4854. The charging stock in the previous case was reduced to a 50 per cent bottoms and then hydrogenolyzed. The hydrogenolate on reduction, in addition to gasoline and gas-oil gave the following lubricating oil cuts:

(1) Medium Motor Oil (overhead)

Yield.....	40 per cent
Gravity.....	25.9
Viscosity at 100° F.....	280 sec.
Viscosity at 210° F.....	49 sec.
Pour.....	40° F.
Flash.....	410° F.
Conradson carbon.....	0.001

(2) Extra Heavy Motor Oil (bottoms)

Yield.....	25 per cent
Gravity A. P. I.....	27.1°
Viscosity at 100° F.....	796 sec.
Viscosity at 210° F.....	74.8 sec.
Pour.....	35° F.
Flash.....	510° F.
Conradson carbon.....	0.18

4855. Treatment of Naphthas for the Elimination of Sulphur and Gumming Tendency. In view of the remarkable facility with which hydrogenolysis eliminates sulphur, natural or cracked naphthas may be treated to advantage. By a mild hydrogen treatment a medium-sulphur, high-gum and unstable gasoline may be rendered stable, with about 50 per cent of the sulphur eliminated under such conditions of operation that the knock rating is raised only to about the same extent as would result from a 7-lb. per bbl. acid treat. This phase of the process would be carried out in such a way that no appreciable change would be made in the boiling range of the naphtha. The process may also be so operated as to eliminate almost entirely sulphur from a high-sulphur, cracked naphtha, with a small increase in knocking tendency. Depending upon conditions of operation, this treatment eliminates from 65 to 98 per cent of the sulphur in the feed stock and gives a gum- and color-stable naphtha which, after a light wash with caustic soda, passes corrosion and doctor tests. The following table shows character of stock charged and finished product. The improvement in color, gum, and sulphur is readily apparent.

Total Product	Smackover Naphtha	Hydrogenated Product (100 Per Cent Yield)
Gravity.....	46.4	51.9
Sulphur.....	0.395 per cent	0.019 per cent
Doctor.....	Does not pass	Passes
Color.....	Straw	+25
I. B. P.....	124° F.	134° F.
Per cent at 212° F.....	14.5	12.0
Per cent at 302° F.....	40.5	45.0
Per cent at 374° F.....	64.0	73.5
Per cent at 400° F.....	71.5	82.0
F. B. P.....	540° F.	502° F.

Gasoline	Smackover Naphtha	Hydrogenated Product (100 Per Cent Yield)
Gravity.....	53.9	55.3
Sulphur.....	0.188 per cent	0.006 per cent
Porcelain dish gum.....	12 mgs.	1 mg.
Copper dish gum.....	21 mgs.	4 mgs.

The change in initial boiling point is due to not fully recovering the low-boiling fractions from the recycle gases.

4856. Production of High-Compression Anti-Knock Gasoline.⁴³ In the case of some of the above examples, hydrogenolysis apparently has served to saturate the hydrocarbon molecule and, to all intents and purposes, to render it more paraffinic. By suitably changing the operating conditions, the effect of this process may be reversed to yield stable but non-paraffinic products. The most important commercial application of this phase at the present time is in the production of anti-knock gasoline from gas-oil. The following serve to show its possibilities:

4857. Charging stock: Cracked distillate from low pressure Tube-and-Tank cracking coils.

Initial boiling point..... 304° F.
Final boiling point..... 430° F.

From this stock there was produced 78 per cent of 400 E. P. naphtha having a knock rating better than Ethyl Aviation Standard. This gasoline is low in sulphur, is gum-stable and water white.

4858. A cut from a highly paraffinic Mid-Continent gas-oil having

Initial boiling point..... 470° F.
Final boiling point..... 584° F.

was hydrogenolyzed to give 82.2 per cent of gasoline with a sulphur content of 0.01 per cent and a knock value such as would require only about 0.15 of a c.c. of lead tetraethyl to make it equal Ethyl Motor Standard. On distillation the gasoline yielded 36 per cent off at 212° F., was water white, and the gum content was 8.4 mgs. Without any treatment it passed doctor and corrosion tests, and was found to be stable on accelerated gum test.

⁴³ The term gasoline (frequently abbreviated to the colloquialism "gas") continues unflinching through the various notable changes which this fuel commodity has undergone since the term was first applied to the light distillates from crude oil. Such distillates, now known as straight run gasoline, originally constituted the only product to which the term was applied. The dearth of straight run gasoline resulted in the development and widespread use of cracking processes, by which means the deficiency of the naturally occurring gasoline was met. Physically, however, the cracked product was different in several respects from the straight run gasoline. It was darker in color and exhibited different boiling characteristics. Chemically the differences were pronounced. The cracked material, or synthetic gasoline, being the product of disintegration of heavy oils, possessed chemical properties remote in many respects from those possessed by the straight-run gasoline. With the advent of processes for the hydrogenation of coal, light motor fuel of dissimilar origin and notably different quality becomes available, yet the term gasoline continues and will continue to be applied to this fuel despite certain physical and marked chemical differences. Evidently the public accepts the term gasoline to define motor spirit as a commodity regardless of origin or differences in chemical composition.

On account of the flexibility of the process, hydrogenation makes possible the substantial duplication of straight run gasoline, if that result is desired.

4859. The same stock was hydrogenolyzed under slightly different conditions to produce 61.5 per cent of a gasoline having a knock rating equal to Ethyl Aviation Standard, containing 0.09 per cent sulphur, with 12½ mgs. of dissolved gum and a fill of 43½ per cent at 212° F. This gasoline also was water white, and gum-stable and passed doctor and corrosion tests without further treatment.

4860. Cracked California gas-oil was hydroformed to produce a highly aromatic anti-knock stock suitable for blending. The charge stock had the following "inspection":

Gravity A. P. I.....	26.2°
Initial boiling point.....	324° F.
Per cent off at 374° F.....	3
Per cent off at 400° F.....	9
Final boiling point.....	598° F.
Aniline point.....	79° F.

The yield from this charge stock was 80 per cent of a finished, water white, gum-stable, blending anti-knock stock of the following "inspection":

Gravity A. P. I.....	42.8°
Initial boiling point.....	90° F.
Per cent off at 212° F.....	16
Per cent off at 284° F.....	35
Per cent off at 356° F.....	70.5
Per cent off at 374° F.....	80.5
Per cent off at 400° F.....	90.5
Final boiling point.....	433° F.
Sulphur, per cent.....	0.016

To equal the knock intensity of this product on a water-cooled test engine, 3½ c.c. of tetra-ethyl lead in a mixture of 70 per cent regular Mid-Continent gasoline with 30 per cent benzol were required. When blended with a poor Mid-Continent stock, it had 75 per cent of the value of benzol as a blending agent.

4861. It will be noted that the gradual development of the hydrogenation of coal and especially of petroleum oils is bringing forth a new terminology. Thus the breakdown of polycyclic or alicyclic complexes under the joint action of high temperature and high hydrogen pressure to form simpler cyclic, e.g., monocyclic compounds, or those from which an aliphatic group has been detached, is appropriately termed *hydrofissioning* (hydroscissioning); the oil so treated is *hydrofissioned* (hydroscissioned). Sometimes hydrofissioning progresses, under special conditions of hydrogen partial pressure, such that little or no extraneous hydrogen appears to become combined and fixed in the liquid products or hydrogenolates. At least the indications suggest that this is the net result. Fissioning under these conditions may be termed *hygestion*. (A contraction of hydrogen digestion.) An oil so treated therefore is *hygested*. In conversion by hygestion a considerable part of the hydrogen may enter into combination with unsaturated gases or fragments thrown off by the liquid hydrocarbons under treatment, yielding gases more or less saturated.

4862. Hydrogen under high pressure possesses the noteworthy power of removing from petroleum hydrocarbons various metalloid compounds which are present. In most petroleum products this *demetalloiding* action is mainly confined to sulphur compounds. Conceivably, however, the same stripping or replacing action could well obtain with respect to compounds of selenium, tellurium, arsenic and other allied bodies to such extent as they might exist in the crude oil. The extraordinary action of high-pressure hydrogen in reacting

on the sulphur compounds of the oil to form hydrogen sulphide, thereby denuding the oil of its sulphur content, may be termed *desulphing*. An oil thus stripped of its sulphur in large measure is *desulphed*. The term should be used, however, particularly to signify a deep-seated removal of sulphur accompanied by a corresponding alteration of the sulphur-containing bodies. The word desulphidation used elsewhere in this text has other connotations both inside and outside the oil industry. The author therefore prefers *desulphed* as a specific term to apply to the removal of sulphur, as hydrogen sulphide, by the hydrogenolysis of

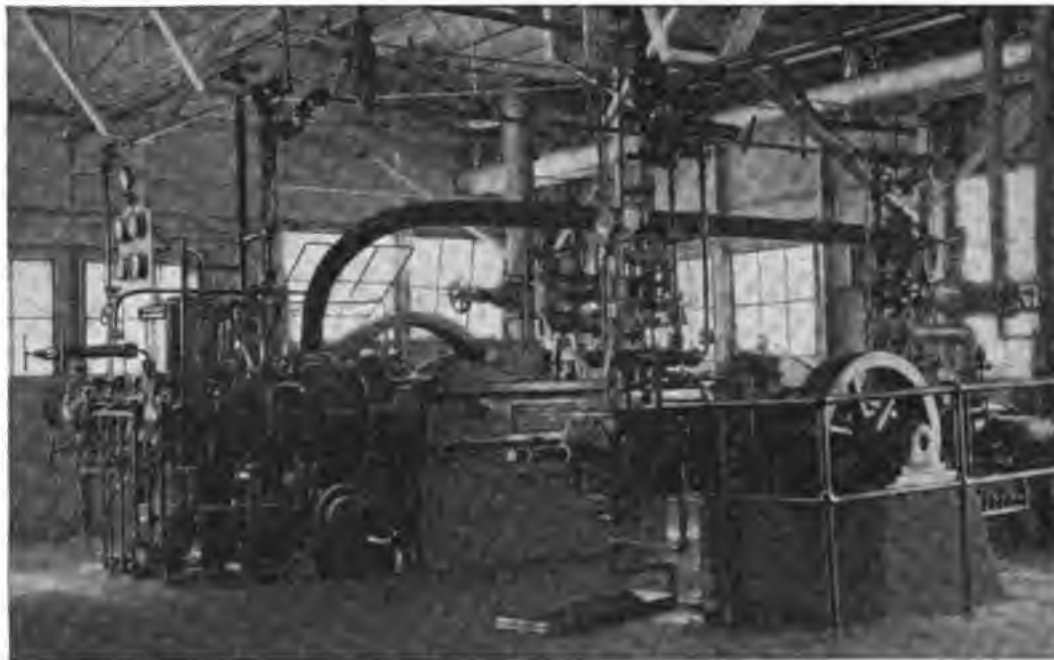


FIG. 112.—HYDROGEN COMPRESSOR SUPPLYING PETROLEUM REACTORS.

the various, and often normally refractory, sulphur compounds present in petroleum.

4863. An oil which has been hydrogen-treated and thus largely stripped of sulphur is "hydrogen-unsulphed," from which have been derived the contractions *hydrunsulph*, *hydrunsulphed* and *hydrunsulphing* used elsewhere in this text: all terms contemplated to be applied in a manner specific to the removal of sulphur by high-pressure hydrogenation.

4864. Other constitutional changes not without import occur in such hydrogenations. Oxygen, as has been noted, is removed, often with marked structural alterations. This would be the case, for example, when the carboxyl group of a naphthenic acid is deoxygenated. Nitrogen compounds in the oil are likely to be attacked with formation of ammonia or its compounds.

4865. Kelber and others (see Chapter XXIX) have used hydrogen to dechlorinate various chlorinated compounds, but these investigations were mostly restricted to comparatively simple reactions in low-pressure catalytic hydrogen

dechlorination of substantially pure substances. High-pressure hydrogenation is far more deep-seated, involving selective phenomena of unusual complexity and reaction orientation singularly responsive to changes in conditions; tending, for example, when applied to a petroleum oil containing the usual multiplicity of bodies carrying sulphur, nitrogen, oxygen, and the like, to expel to a surprising degree such elements, thereby to provide, at low cost for industrial purposes, relatively pure mixed hydrocarbons.

4866. Broadly speaking, petroleum is considered to be a mixture of hydrocarbons. In a strict analytical sense, however, the composition is far more complex. Mercaptans, aldehydes, carboxylic acids, nitrogen compounds and numerous other bodies not classed with hydrocarbons are likely to be present. Among other effects, high-pressure hydrogenation of petroleum and its distillates exerts a *hydrocarbonizing* action. The change thus may be contemplated as a unifying reaction in the sense of conversion or elimination of non-hydrocarbon bodies from the liquid constituents of petroleum fractions, a result of enormous commercial significance. *Hydrocarbonized* petroleum (paradoxical though the term sounds) thus has made its advent with the development of certain phases of high-pressure hydrogenation.

4867. In the light of the foregoing, the convenient terms *hygested*, *hydrunsulphed* and *hydrocarbonized*, appropriately used in the petroleum industry, appear reasonably self-explanatory and desirably concise.

4868. Hydrogenolysis. The unique action of hydrogen of extrinsic origin under high pressures and high temperatures on petroleum gives rise to the descriptive term *hydrogenolysis*, a term frequently used in the foregoing text. Misapprehension in the past respecting the character of such action has caused a laxity of expression which warrants correction. The established term "destructive hydrogenation" doubtless can be bettered, since it seems scarcely to do justice to the selective control and orderly procedure of petroleum hydrogenation conversion in its various feasible commercial adaptations; perhaps, even suggesting the possibility of the inception of cracking conditions. This last assumption, as the author has previously noted, is far from the truth. Pyrolytic cracking is a haphazard breakdown and partial recombination by the agency—heat. The trend is towards dehydrogenation with formation of asphaltic polymers and carbon.

4869. The most careful regulation of temperature and pressure in pyrolytic cracking tends towards differences only in degree rather than in kind. Hydrogenolysis, with its favorable exothermic transitions, provides sharp differences in kind. For example, sulphur, a recognized dehydrogenating agent ever present in crude petroleum, undoubtedly is disturbingly active in this pyrolysis, while in hydrogenolysis sulphur compounds apparently are selectively attacked with removal, to an astonishing degree, of the sulphur as hydrogen sulphide, from the zone of hydrogenation, thus curtailing dehydrogenating influences.

4870. In such pyrolysis asphaltic bodies ordinarily are among the first to become carbonized. In hydrogenolysis the reverse holds true. An oil, black with asphaltic impurities, changes to a light-colored product as hydrogen recon-

stitutes the asphalts to colorless oils. The haphazard rearrangements of pyrolytic decomposition are replaced, in hydrogenolytic decomposition, by a far more orderly and useful reconstitution. Given the proper conditions, hydrogen becomes an avid reactant dominating and suppressing the fortuitous changes normal to pyrolysis. Hydrogenolysis, therefore, should not be confused with pyrolytic cracking.

To the petroleum oil refiner, accustomed as he is to the coking action of cracking, there is something magical in the manner hydrogen gas acts, especially on black tarry oils. He sees a dark-colored asphalt-containing oil fed into a hydrogenator and finds it emerging as a colorless product, usually with actual volu-

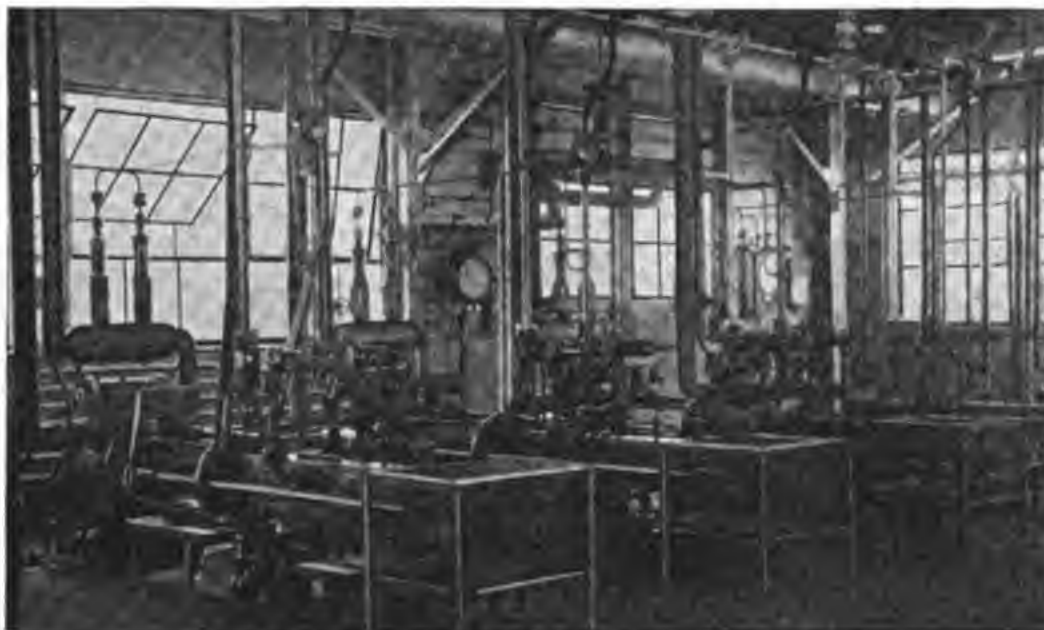


FIG. 113.—PORTION OF PUMP ROOM IN PETROLEUM HYDROGENATION PLANT.

metric gain. He contrasts the crudities of cracking with this more scientific approach to a solution of one of our most important fuel problems, and, despite the greater cost of plant, the higher pressures involved and the more skillful control required, he recognizes that an important forward step has been taken.

4871. Other high pressure treatments of carbonaceous raw material call forth such terms as *nitrogenolysis*, applicable to its decomposition in an atmosphere of nitrogen; *carbolytic*, where the diluent atmosphere is an oxide of carbon, and *aquolysis*, where water vapor, especially at temperatures and pressures above the critical, is the diluent.

4872. Reference has been made above to the hydrogenolysis of mixtures of coal and oil, especially to the greater ease of handling mixtures which can be pumped nearly as easily as oil. Other advantages, residing in the quality of the hydrogenolates are attributed to the hydrogenolysis of these mixtures.⁴⁴ Coal and its tars are stated to yield spirits of high anti-knock value which are deficient in constituents boiling below 100° C. Products of the

⁴⁴ I. G., Brit. Pat. 296,984, Aug. 22, 1928; *Brit. Chem. Abst.*, 1930, 48B; *Chem. Abst.*, 1929, 5306; French Pat. 659,907, Sept. 3, 1928.

needed low boiling point but of not as high an anti-knock value are obtained from petroleum. The hydrogenolysis of mixtures of coal and oil therefore yields a well balanced fuel.

4873. Highly Purified Petroleum Oils. A crude petroleum or heavy fraction is hydrogenated by treatment with hydrogen at a high temperature and pressure (suitably about 400–450° and 50–100 atmospheres with Pennsylvania crude oil) and a product of the desired viscosity is separated and further purified.⁴⁵ Catalysts such as oxides of chromium and molybdenum may be used in the process.

4874. In an apparatus for cracking and hydrogenating oils and other carbonaceous materials, the oil is circulated through a reaction vessel and heating coil.⁴⁶

4875. Crude oil or coal paste is destructively hydrogenated, part of the products being cracked and the undesired or unchanged liquid products returned to the hydrogenation stage. Treatment of an oil containing 86 per cent boiling above 300° C. and 14 per cent boiling between 200–300° C. gave a product containing 20 per cent of gasoline and 30 per cent of middle oil. The latter on cracking yielded 37 per cent of gasoline, 45 per cent of middle oil, and a residue which was returned for rehydrogenation.⁴⁷

⁴⁵ Howard (to Standard Oil Development Co.), Brit. Pat. 308,297, March 21, 1928; *Chem. Abst.*, **1930**, 234.

⁴⁶ Standard Oil Development Co., French Pat. 667,177, Jan. 9, 1929; *Chem. Abst.*, **1930**, 1212.

⁴⁷ Kamm, Adams, and Imperial Chemical Industries, Ltd., Brit. Pat. 325,487; *Chem. Age* (London), **1930**, 398; *Brit. Chem. Abst.*, **1930**, 450B.

CHAPTER XLIX

HYDROGENATION OF MINERAL OILS (II) INCLUDING LOW PRESSURE HYDROGENATIONS¹

4900. The simple hydrogenation, or the more involved processes of hydrogenolysis, of mineral oils is a subject that, in its present condition, lends itself but ill to systematic treatment. In the first place the reactions in many cases are obscure. Secondly, the "literature" of the subject available at the present time consists, for the most part, of patent specifications and of a few articles of a very general character. Included herein, however, are all those references to hydrogenation even though casual and remote which have come to the author's attention. The treatment here will, perforce, be little more than a more or less systematic arrangement of proposed processes.

4901. In cracking petroleum oils in the presence of hydrogen, Whitaker and Leslie² have reached the following conclusions:

1. That effects often ascribed to catalysis are in reality due to effective heat transfer by conduction and convection from the large heated surfaces exposed to the gases.

2. That hydrogen is produced from an oil even when the cracking takes place in hydrogen.

3. That considerable absorption of hydrogen takes place when an oil is cracked in an atmosphere of hydrogen, and this absorption is greater the higher the concentration of hydrogen, the higher the temperature (within the range studied), and the lower the oil rate.

4. That no marked and consistent difference in the amount of tar formed when an oil is decomposed alone or in hydrogen at temperatures of 723° C. or below is noticeable. At 825° C. less tar is formed when the oil is cracked in hydrogen. The tars formed below 723° C. are in large part unchanged or partly changed oil, whereas those tars formed above 800° C. are essentially composed of synthetic products.

5. That the reactions which result in decreasing the proportion of illuminants are the most rapid.

¹ In abstracting patents and describing inventions that part only of each invention which is relevant to our subject-matter is dealt with. Originally it was the intention to place all matter relating to berginization, or to analogous processes, whether applied to mineral oils, to coals, or to tars, in Chapters XLIV to XLVIII, but with the expansion of the text through the attempt to include the majority of the proposals in the hydrogenation field the line of demarcation between these chapters and those immediately succeeding unfortunately has been lost.

² *J. Ind. Eng. Chem.*, **1916**, 694.

6. That the presence of hydrogen during the decomposition of an oil has the effect of increasing largely the proportion of the carbon of the oil appearing as hydrocarbons in the gas.

7. That with correct design of apparatus, and proper adjustment of temperature, rate of oil feed, and concentration of hydrogen it is possible to obtain gases of widely varying compositions.

4902. The results of experiments by Winkler³ on the problem of motor gasoline are of interest. Winkler observes that California petroleum is one of the large sources for gasoline, and yet that probably 80 per cent of it is too thick for any explosive mixture and "a sootless burn" in the cylinder. To depolymerize the heavy hydrocarbon oils down to their simplexes in a manner somewhat analogous to the depolymerization of synthetic rubber back to isoprene—the following experiments were carried out:⁴

4902A. 1. Effect of Corona. A glass tube 2½ in. diameter by 3½ ft. long, wrapped with wire gauze, with a ½-in. copper rod suspended co-axially through its center, was used as a hot vapor chamber, while at the same time the inside rod and outside gauze were kept at a potential of from 25,000 to 30,000 volts by dynamo and high potential transformer. When the room was darkened, a continuous bright bluish glow was evident throughout the tube, i.e., a corona. Through this glow (air removed) various California heavy distillates were distilled repeatedly, with a large excess of hydrogen (dry and moist), the object of the corona being to ionize the hydrogen. (The dielectric constants of hydrogen and hydrocarbon vapors and air were found to be not very different.) Practically no change could be detected in the oils after repeated slow distillations through the above chamber.

2. Effect of Arc. The Birkeland-Eyde process was applied to these oils in an atmosphere of hydrogen. The oils, both liquid and gaseous, were passed through with increasing speed, to shorten the time in the arc. The carbons were hollow, and hydrogen was passed inward through both. They were kept cool by a water jacket. The results were variable, but in every case the oils were reduced to non-condensable gases and a cloud of fine carbon.

3. Effect of Steam and Aluminum under Pressure. Very fine aluminum dust was mixed with various heavy California oils to a "suspension," and these mixtures subjected to a pressure of 110 lb. per sq. in. with steam in a heavy, specially constructed retort. They were also agitated, and at the same time heated to various temperatures up to their cracking points. The purpose of the aluminum and steam was to generate nascent hydrogen within the oil. A variety of attempts indicated no success. The aluminum was not amalgamated.

4. Effect of Reduced Nickel Oxide and Hydrogen on the Aerated Oil. According to Charitschkoff, better results at cracking Russian petroleum were obtained by first oxidizing the oil.⁵ Heavy California oils were heated and aerated (by drawing air through them) for two or three days, to oxidize them and to generate petroleum acids (the purpose of this oxidation also being to introduce carboxyl groups, with the possibility of splitting out water with the hydrogen afterwards, and leaving the rest of the broken molecule to unite with the excess hydrogen).⁶ The aerated oils were subjected to the action of reduced nickel oxide and hydrogen, but without success. Iodine was substituted for the nickel oxide with no better results.⁷

5. Effect of Rhodium-Black and Hydrogen. Active platinum-black, made according to the Loew process,⁸ has been shown to be a good catalyst to hydrogenate pure benzol and pure benzene. It is, however, poisoned by sulphur bodies.⁹ California oils contain sulphur,

³ *J. Franklin Inst.*, 1914, 178, 97.

⁴ *Z. angew. chem.*, 1913, 609.

⁵ *Petroleum*, 1913, 748.

⁶ *Z. angew. chem.*, 1913, 561-606.

⁷ Ramsay found nickel in all crude oil examined and suggests that it may have acted as a catalyst in the formation of petroleum from gases of low molecular weight. *J.S.C.I.*, 1923, 43, 470; *J. Inst. Petrol. Tech.*, 1924, 10, 87.

⁸ *Ber.* 23, 289.

⁹ *Ibid.*, 45, 1471.

and do not hydrogenate under these conditions. Bredig has shown that rhodium metal acts as a catalyst to break down formic and acetic acids to hydrogen and carbon dioxide, etc., and that sulphur bodies are favorable to its activity.¹⁰ Rhodium-black was made (by the Loew process), and tried out on California oils under parallel conditions, but failed to hydrogenate in the least.

4903. Rittman observes that many inventors have made claims to processes of hydrogenation of petroleum oils in connection with their method of cracking. In most of these cases the hydrogen is derived from steam which is admitted with the oil or else is derived from the hydrocarbons themselves by employing a suitable catalyzer.¹¹

4904. Tests conducted by Cross with many catalytic bodies including aluminum powder, nickel, copper, mercury, zinc dust, iron dust, and platinized pumice did not afford increased yields of light hydrocarbons from heavier oils.¹²

4905. Brooks, Bacon, Padgett and Humphrey¹³ state that the effect of pressure in diminishing the percentage of olefines in the gasoline obtained is a noteworthy feature of their work. The same effect is very strikingly shown in the interesting results of Whitaker and Rittman on the effect of pressure in the yield of illuminants in oil gas. At 900° C., Whitaker and Rittman obtained from a given quantity of oil 122 liters of illuminants at 0.75 lb. pressure, 50 liters at atmospheric pressure and 15.5 liters at 45 lb. (absolute) pressure. They were also able to show that at temperatures of 750° to 800° C. the addition of hydrogen to the gas mixture has the effect of partially hydrogenating the olefines and that this reaction takes place more readily as the pressure on the system is increased. Ipatiev¹⁴ has made the interesting observation that, in the distillation of petroleum under pressure, at higher pressures the evolved gases become continually poorer in hydrogen in spite of the higher temperatures required to maintain the higher pressures. The pressures employed by Ipatiev were 120 to 340 atmospheres.

4905A. The liberation of hydrogen from petroleum hydrocarbons at various temperatures has been studied by Engler¹⁵ and his student. They obtained no hydrogen below 470° at atmospheric pressure from kerosene fractions boiling below 280° C. The liberation of hydrogen from different hydrocarbons at a given temperature depends somewhat on their constitution. Thus, benzene yields appreciable quantities of hydrogen only at temperatures above 500° C.

The work of Brooks, Bacon, Padgett and Humphrey indicates that if hydrogenation of the liquid olefines takes place during distillation under pressure, it occurs simultaneously with their initial formation. A sample of cracked naphtha, having an iodine number of 55.0 was heated to 196° C. with hydrogen for thirty hours under 3000-lb. pressure per sq. in. The iodine number and refining loss with sulphuric acid were practically unaffected, the iodine number of the final product being 52.9. Results closely parallel to this were obtained by Rhodes, working with liquid fatty oils. The apparatus employed was a steel bomb connected with a solenoid stirrer constructed as described by Stuckert and Enderli.¹⁶ Ueb-

¹⁰ *Oest. Ch. Ztg.*, No. 14, 1911, 266.

¹¹ *Bulletin 114*, Bur. of Mines, 24.

¹² *Petroleum, Asphalt and Natural Gas Bulletin*, No. 14, Kansas City Testing Laboratory, 97.

¹³ *Ind. Eng. Chem.*, 1915, 180 and 412.

¹⁴ *Ber.*, 1904, 2969.

¹⁵ Engler and Hofer, *Das Erdöl*, 1, 574.

¹⁶ *Zeitschr. f. Elektroch.*, 1913, 570.

belohde and Woronin¹⁷ showed that in the presence of nickel, hydrogen was split off from a Baku crude oil at as low a temperature as 180° C. The results of Zelinski,¹⁸ i.e., dehydrogenation at temperatures above 300° C. in the presence of platinum are to be expected. Ostromislenski and Bujanadse¹⁹ showed that in the presence of nickel a Russian crude oil gave only coke, 40 per cent, and gas at temperatures between 660° to 700° C., no tar or liquid being obtained at all. Furthermore, the gas contained 72 to 75 per cent of hydrogen and the remainder consisted of saturated hydrocarbons. These facts are quite significant in view of the proposed cracking processes of Vernon-Boys, Lamplough and others, who introduce nickel into the cracking zone. A series of experiments was made by Brooks, Bacon, Padgett and Humphrey at atmospheric pressure and at temperatures of 500° to 550° C., employing various catalytic substances. Kerosene and solar oil vapors passed through an iron tube containing burned clay, carbon, coarse and finely divided iron, coarse and finely divided copper, heated to the above-named temperature, yielded gasoline fractions, which showed an olefine content of approximately 25 to 30 per cent. When nickel was employed the proportion of olefines in the gasoline product was 48 per cent.

4906. Ellis and Wells describe the results of experiments with several forms of tubular cracking apparatus and the hydrogenation of some of the products obtained.

Using kerosene of 42° Bé. (sp. gr. 0.814) yields of gasoline (boiling-point up to 150° C.) of 18 to 20 per cent were obtained at 450° to 600° C. By distilling off the gasoline and retreating the residue, and also scrubbing the gaseous reaction products with oil, yields of 40 to 45 per cent of gasoline were obtained. The gasoline was denser than normal gasoline of the same boiling-point, had a higher refractive index and was unsaturated; the iodine value of the distillation fractions was higher the lower the boiling-point, a fraction boiling below 70° C., for example, having an iodine value of about 300. On standing for a long time the gasoline became darker in color, and when subsequently distilled, a violent reaction occurred at about 160° C., resulting in the production of a dark brown viscous oil. A similar reaction occurred at about 110° C. on distilling under diminished pressure (6 to 10 mm.). The viscous polymerized product reacted violently with sulphur and with sulphur chlorides, a viscous oily mass being produced. Hydrogenation improved the odor of the gasoline, changed the color from light straw-color to water-white, and destroyed the tendency to polymerize.²⁰

4907. The Desirability of Unsaturated Hydrocarbons. According to Brooks²¹ the idea that it is always a good thing to hydrogenate unsaturated hydrocarbons, is erroneous. In respect of odor there is nothing gained and in lubricants more not less of unsaturated hydrocarbons would be advantageous.

4908. Nevertheless petroleum spirits containing di-olefines, such as are produced by cracking, are especially liable to deposit resinous condensation products on storage analogous, presumably, to caoutchouc formed from isoprene. Hydrogenation in the liquid phase may be expected to reduce refining losses. Possibly the removal of sulphur-containing impurities would be a condition precedent, as it was in the case of naphthalene.

4909. Olefines More Resistant to Hydrogenation than Fatty Acids. According to Brooks and Humphrey, the unsaturated fatty acids are much easier hydrogenated than are the unsaturated hydrocarbons. The first surmise was that the petroleum olefines contained traces of sulphur compounds, which poisoned the

¹⁷ *Petroleum*, Berlin, 1911, 7.

¹⁸ *Ber.*, 1912, 45, 3678.

¹⁹ *J. Russ. Phys. Chem. Ges.*, 1910, 195.

²⁰ *J. Ind. Eng. Chem.*, 1915, 1029; *J.S.C.I.*, 1916, 102.

²¹ *Chem. & Met. Eng.*, 1921, 1023.

catalyst, but a mixture of cottonseed oil and highly unsaturated kerosene, iodine number 55.2, purified by distillation over fine copper oxide yielded a semi-solid mixture of solid hydrogenated cottonseed oil and the kerosene practically unchanged.²²

4910. Formation of Aromatic Hydrocarbons from Natural Gas Condensates. Davidson.²³ Natural gas was cracked in presence of metals. Nickel, iron and cobalt markedly accelerated the production of carbon and hydrogen, and hindered the formation of aromatic hydrocarbons.

PROCESSES INTRODUCING STEAM

4911. In the cracking process of Valpy and Lucas,²⁴ steam is superheated to a temperature slightly below the cracking-point and is sprayed into the oil in a still. The mixture of oil, vapor and steam is passed through heated catalyzing tubes of nickel, which may be packed with catalyzing material, and then to a coil in the oil still where the heat of the cracked vapor is utilized for heating the oil. The catalyzing tubes may be heated electrically, or by an oil burner.²⁵

4912. A modification of this method of cracking oil of Valpy and Lucas,²⁶ consists in removing oil vapor from a still by means of steam or an inert gas under pressure and bringing the mixture into contact with a heated catalyst, such as nickel or one of its alloys, or "nickel suboxide" or oxide; the pressure of the mixture after leaving the catalyzing chamber is reduced suddenly. The light oils produced are condensed.²⁷

4913. A catalyst for cracking petroleum oils described by Lucas²⁸ is prepared by heating a mixture of oxides and oxalates of iron and nickel, chromium or cobalt to a sintering temperature with small amounts of carbon and aluminum, magnesium or cerium to reduce the metallic compounds. The metallic catalyst thus formed retains its efficiency in continued use for cracking oils for a considerable time.

4914. A description by Ramage²⁹ may relate to a hydrogenation process. A hydrocarbon vapor similar to the lighter fractions of casing head gasoline is mixed with steam and the mixture is brought into contact with ferrous oxide at a temperature of 600° C. or higher, in order to form a fuel for internal-combustion engines.³⁰

4915. Palmer³¹ describes what is, primarily, an oxidation cracking process. Mention is made, incidentally, of the production of hydrogen from steam introduced and to the action of this hydrogen in saturating some unsaturated compounds.

4916. According to Weaver³² oil is passed through a pipe still, in which it is heated to 370°, at about 2 atmospheres, into an expander, where heavy residues are removed, and a converter, in which it is mixed with steam and led at about 600° over ferric oxide. The oil cracks, and the unsaturated products take up hydrogen from the steam. The issuing vapors are rapidly cooled to 235° by treatment with fresh, uncracked oil, at which temperature most of the carbon present separates. The fresh oil and the high-boiling constituents of the cracked products are passed to the still.³³

4917. Anti-knock Gasoline by Wade Process.³⁴ Gas-oil is atomized by steam at 350° F. (176° C.) into a coil 120 ft. long which is maintained at 1250° F. (676° C.); at the end of this the vapors come in contact with a nickel chromium catalyst, dissociation and recombination take place with the production of a gasoline ("Wadolene") which has anti-knock properties and is stated to be free from sulphur.

²² *J. Am. Chem. Soc.*, 1918, 842.

²³ *J. Ind. Eng. Chem.*, 1918, 10, 901.

²⁴ *Brit. Pats.* 20,470, Sept. 10, 1913, and 2838, Feb. 3, 1914.

²⁵ *J.S.C.I.*, 1915, 71.

²⁶ *Brit. Pats.* 12,653, May 22, and 18,923, Aug. 21, 1914.

²⁷ *J.S.C.I.*, 1915, 707.

²⁸ *U. S. Pat.* 1,168,404, Jan. 18, 1916.

²⁹ *U. S. Pat.* 1,687,890, Oct. 16, 1928, to Ramage (assigned to Gyro Process Co.).

³⁰ *Chem. Abst.*, 1929, 23, 274.

³¹ *U. S. Pat.* 1,699,627, Jan. 22, 1929.

³² *U. S. Pat.* 1,601,786, Oct. 5, 1926, assigned to Oil Products Co.

³³ *Brit. Chem. Abst.*, 1927, B6.

³⁴ *Refiner*, 1926, 5, No. 11, 24; *Petrol. Times*, 1926, 16, 94; *Chem. Abst.*, 1927, 21, 2378.

4918. Coast mixes petroleum oil, natural gas and steam and subjects the mixture to pressure at a cracking heat. By mixing the steam and gas with the oil, a much "sweeter" and better product (gasoline) is obtained and the yields are found to be improved.³⁵

4919. Zerning passes a mixture of heavy petroleum and water (1 part water to 6 to 10 parts oil) first through a heater to raise the temperature of the mixture to 300° to 400° C., then through tubes at a dull red heat, condenses and passes the gases from the condensers under pressure into a body of petroleum at ordinary temperature, from which gasoline is subsequently recovered by distillation.³⁶

4919A. Stone ^{36a} claims to obtain a gasoline mixture including benzol and toluol by heating heavy oil and water under pressure at about 315° C. in presence of a nickel-chromium catalyst.

4920. It seems doubtful if, in the processes next to be mentioned, the function of the metallic oxides is exclusively catalytic. Porges and Stransky increase the volatility of hydrocarbons in the following way: the vapors of the latter, mixed with steam, at a temperature below 600°, are brought into contact with metallic oxides such as the oxides of lead and nickel which function as catalyzers. A portion of the hydrocarbon is converted into carbon dioxide by reduction of the metallic oxide which is regenerated by means of air or oxygen.³⁷

4921. A process and apparatus for converting heavy into light hydrocarbons is described by Porges, Stransky and Strache. A mixture of the vaporized oil and steam is passed over a catalyst (iron oxide or oxide of another metal capable of forming several oxides), which is heated to 500° to 600° C., and light products are formed. When the hydrocarbons begin to diminish the catalyst is regenerated by heating it in a current of air or oxygen.³⁸

4922. Hydrogenation and Cracking: Steam and Hydrocarbon Over Coke.³⁹

The Forwood and Tapley process is for hydrogenation and cracking of hydrocarbon oils for the production of motor spirit by processes in which the hydrocarbon vapors mixed with steam are passed over heated carbon, such as charcoal derived from wood-peat or other vegetable or animal matter. The invention consists in treating paraffin oil, boiling 140°–320°, at temperatures of 550°–600°; kerosene, boiling 180°–350°, at 600°–630°; solar oil, boiling 230°–370°, at 650°–700°; creosote oil, boiling 180°–270°, at 650°–750°; anthracene oil, boiling 270°–400°, at 750°–800°; and heavy paraffin oils, used as fuel, at 850°–950°.⁴⁰

4923. Gyro Vapor Phase Cracking. According to Osterstrom ⁴¹ in the Gyro process as worked at Cabin Creek, West Virginia, the hydrocarbon vapors, mixed with steam, pass through tubes at 2000° F. (1093° C.) and here come into contact with axially placed masses of iron oxide imbedded in concrete. Osterstrom surmises that the hydrogen from the dissociated steam may form new compounds with the unsaturated products of cracking. It would be surprising if it were so, for at such temperatures one would expect dehydrogenation to prevail.⁴²

4924. Cracking and Hydrogenation of Shale Oil. Forwood's process ⁴³ for the cracking and hydrogenation of hydrocarbon oils has practicable application to the treatment of shale oils. When shale is distilled for the recovery of hydrocarbon oils the spent shale is still carbonaceous, the carbon content being in the form of actual carbon or, at any rate, capable of decomposing steam at the right temperature. If, therefore, steam and hydrocarbon vapors are passed over the spent shale at 550° C. to 600° C., the hydrocarbon vapors are cracked, hydrogen-containing gases are formed, and these, reacting with the unsaturated constituents of the

³⁵ U. S. Pat. 1,252,401, Jan. 8, 1918.

³⁶ U. S. Pat. 1,183,266, May 16, 1916.

^{36a} French Pat., 495,794, July 11, 1919.

³⁷ Ital. Pat. 142,453, May 30, 1914; *Chem. Abst.*, **1915**, 2814.

³⁸ Brit. Pat. 11,420, May 8, 1914; *cf.* U. S. Pat. 1,205,578, Nov. 21, 1916, to Strache and Porges.

³⁹ Brit. Pat. 145,198, Apr. 16, 1919 to Forwood and Tapley.

⁴⁰ *Chem. Abst.*, 1920, 3153. The process is stated in general form in Brit. Pat. 133,059, Dec. 12, 1916, to the same patentees; also in U. S. Pat. 1,440,286, Dec. 26, 1922, to Forwood.

⁴¹ *Oil and Gas Jour.*, **1928**, 226.

⁴² A modification of the Gyro cracking process is in operation at Newark, Ohio.

⁴³ U. S. Pat. 1,523,942, Jan. 20, 1925.

hydrocarbon mixture will hydrogenate the latter. Apparently the hydrogenation takes place either because the hydrogen is nascent, or because the spent shale acts catalytically, or for both these reasons.

4925. The process may be divided, that is, it may be one of simple hydrogenation, or of combined cracking and hydrogenation, or, again, of combined distillation, cracking and hydrogenation. The simple hydrogenation is usually conducted as follows: a retort (usually, but not necessarily vertical) is filled with spent shale and the shale is heated to 450°–600° C. Superheated steam and oil of 150° C. maximum boiling-point, are admitted at the top and the products—oil, excess steam and gas—removed by a pipe at the bottom. The oil, etc., pass through condensers and washers. A door is provided in the retort whereby, from time to time, the exhausted mineral residue of the shale may be removed. A comparison of the liquid product with the original oil is given in the following table:

Oil before Hydrogenation. Began to distil at 63° C.		Oil after Hydrogenation. Began to distil at 18° C.	
Distilling, Degrees C.	Volume, Per Cent	Distilling, Degrees C.	Volume, Per Cent
Below 100	7.0	Below 100	20.5
Below 110	17.0	Below 110	39.0
Below 120	37.0	Below 120	55.5
Below 130	64.5	Below 130	77.5
Below 140	82.0	Below 140	89.5
Below 150	100.0	Below 150	100.0
Hydrocarbons	Volume, Per Cent	Hydrocarbons	Volume, Per Cent
Unsaturated.....	62	Unsaturated.....	17
Aromatic.....	27	Aromatic.....	47
Paraffin.....	11	Paraffin.....	26

The scrubbed permanent gas may be used to heat the retort.

4926. In carrying out the combined cracking and hydrogenation process a vertical retort is filled with broken, spent shale and heated to 600° C. Crude shale oil, boiling between 180° and 220° C. is passed, with excess of superheated steam, upwards through the shale. The products passing out at the top are condensed, scrubbed, etc., as usual. A comparison between the liquid product and the original oil is shown in the following table.

Oil before Hydrogenation. Began to distil at 150° C.		Oil after Hydrogenation. Began to distil at 32° C.	
Distilling, Degrees C.	Volume, Per Cent	Distilling, Degrees C.	Volume, Per Cent
Below 150	None	Below 100	5.0
		Below 110	8.0
		Below 120	10.0
		Below 130	30.0
		Below 140	60.0
		Below 150	96.0
Below 180	100.0	Above 150	4.0
Hydrocarbons	Volume, Per Cent	Hydrocarbons	Volume, Per Cent
Unsaturated.....	69	Unsaturated.....	24
Aromatic.....	21	Aromatic.....	38
Paraffin.....	10	Paraffin.....	38

4927. The third method, combining distillation of the crude shale, cracking and hydrogenation in one operation involves a modification in the construction of the retort. There must be a door at the top for charging fresh shale and another, at the bottom, for removing exhausted shale. The upper part of the retort is heated to 400° C. and the lower part to 600° C. Near the top, or somewhat lower, superheated steam is admitted. This mixing with the steam and hydrocarbon vapors distilling from the fresh shale is carried down to the cracking and hydrogenating zone as before. The table shows the difference between straight shale oil and that produced by the third method.

(a) Shale Oil produced during an ordinary Retorting of the Shale at about 420°-450° C. Began to distil at 70° C.		(b) Oil produced during the Retorting of the Shale at about 420° C., and subsequent Cracking and Hydrogenating at about 580°-600° C. Began to Distil at 38° C.	
Distilling, Degrees C.	Volume, Per Cent	Distilling, Degrees C.	Volume, Per Cent
Below 100	1.0	Below 100	18.0
Below 110	1.5	Below 110	29.5
Below 120	2.0	Below 120	39.5
Below 130	2.5	Below 130	53.0
Below 140	3.0	Below 140	71.0
Below 150	3.5	Below 150	86.0
Below 160	4.0	Below 160	91.0
Below 170	9.5	Below 170	93.0
Below 180	13.5	Below 180	95.0
Below 190	19.0	Below 190	97.5
Below 200	23.0	Above 200 (pitch)	1.0
Below 210	27.0		
Below 220	27.5		
Below 230	30.0		
Below 240	32.0		
Below 250	35.0		
Below 260	39.0		
Below 270	42.0		
Below 280	46.0		
Below 290	50.0		
Below 300	54.0		
Below 310	61.0		
Below 320	64.0		
Below 330	66.0		
Below 340	67.0		
Below 350	76.5		

NOTE.—The residue of 23.5 per cent distilling above 350° C. was pitch.

(a) Shale Oil produced during an ordinary Retorting of the Shale at about 420°-450° C.		(b) Oil produced during the Retorting of the Shale at about 420° C., and subsequent Cracking and Hydrogenating at about 580°-600° C.	
Hydrocarbons	Volume, Per Cent	Hydrocarbons	Volume, Per Cent
Unsaturated.....	66	Unsaturated.....	9
Aromatic.....	12	Aromatic.....	40
Paraffin.....	22	Paraffin.....	51

4928. White ⁴⁴ describes a process which is rather a decarbonization than a primary hydrogenation. The oil or residue, with or without preliminary distillation, is distributed in a liquid state, and without the addition of steam, on to the surface of quicklime which has been heated to 500°–600° C. in a retort or chamber. The vapors of lower boiling-point thus produced may be drawn off by suction and fractionated. Crude paraffin oil thus treated yields 20 to 25 per cent of hydrocarbons with flash-point and boiling-point similar to those of gasoline. The lime may be regenerated by burning off the deposit of carbon.⁴⁵

4929. Sabatier and Mailhe,⁴⁶ in an essentially decarbonization process, pass oil vapors over a catalyst at temperatures between 400° and dark red heat. They prepare the catalyst of finely divided metal or metals, or metallic oxides or salts that can be reduced to form divided metal, together with neutral refractory substances free from silica and an agglutinant free from silica. Suitable refractory materials are magnesia, alumina, bauxite, lime, baryta, strontia, or the corresponding carbonate, or graphite. Suitable agglutinants are glue, dextrin and starch. Examples of such compounds comprise: (1) iron filings, magnesium oxide and dextrin; (2) oxide of iron, magnesium, bauxite and glue; (3) finely divided iron, alumina and dextrin. The resulting compounds are moulded and dried and packed into cracking tubes composed of metal or earthenware lined with a non-siliceous coating. When the catalyst loses its activity by reason of the deposition of carbon, it is revived by the passage of steam, a gaseous mixture of hydrogen, carbon monoxide and carbon dioxide being produced. This gas can be utilized as a reducing agent or fuel, the carbon dioxide being removed by washing if necessary. The metallic oxide formed by the steam, and the oxide used in making the catalyst initially, are reduced to metal by means of hydrocarbon vapors. The volatile portion of the products of the cracking operation, namely, that distilling below 150°, is treated for the removal of the malodorous unsaturated compounds by reduction with hydrogen in the presence of finely divided metals at 150° to 300°.

4930. Tars and mineral oils are treated for the production of benzene, toluene, gasoline, etc., by heating them in a closed vessel under pressure and allowing the vapors formed to expand when the requisite temperature and pressure have been reached. In the case of tar, temperatures between 90° and 450° and pressures between 2 and 18 kg. per sq. cm. are used. The vapors obtained in one autoclave may be injected into a second autoclave containing tar or oil under a different pressure and temperature. The finely divided nascent carbon which separates acts as a catalyst, the nascent hydrogen also entering into reaction.⁴⁷

4931. Hall cracks oils for the manufacture of motor spirit by heating the vapors of the heavy hydrocarbons under pressure in the presence of a catalyst capable of affixing hydrogen to hydrocarbons, then allowing the vapors to expand and deposit carbon, and finally condensing the vapors with or without preliminary dephlegmation or subsequent distillation. The operation may be conducted under a pressure of 5 atmospheres and at a temperature of 600° and upwards. Gas-oil treated in this way yields 50 to 70 per cent of oil of sp. gr. 0.765 suitable for gasoline engines. Metals such as nickel, cobalt, silver, palladium, chromium or manganese, or their oxides, may be used as catalysts. In one form of apparatus the oil passes through a preheater into a converter consisting of tubes containing cylindrical nickel rods, and the products escape through a reducing-valve into an expansion chamber, fitted with a metallic gauze screen and thence to a condenser. The unsaturated materials formed during the process are claimed to be saturated with hydrogen which is derived from the oil itself. No water, steam, hydrogen or outside source of hydrogen is used.⁴⁸

4932. By another modification of the Hall process motor spirit is produced by passing a kerosene fraction boiling up to about 220°, from which the gasoline has been removed, between minute interstices under very high pressure, such as 1000 to 3000 lb. per sq. in., in the presence of hydrogen, coal gas, or other gas containing free hydrogen or a hydrocarbon gas such as ethylene or oil gas, and at a temperature not above the lowest boiling-point of the liquid, e.g., 100° to 120°. Combination of the gas and oil is said to take place. Suitable apparatus comprises a series of discs or plugs, preferably nickel between or through which the liquid is forced. The discs or plugs may be scratched to form fine grooves.⁴⁹

⁴⁴ Brit. Pat. 5,434, Mar. 3, 1914.

⁴⁵ J.S.C.I., 1915, 651.

⁴⁶ Brit. Pat. 16,791, July 14, 1914; *Chem. Abst.*, 1916, 273; U. S. Pat. 1,152,765; *Chem. Abst.*, 1915, 2814.

⁴⁷ Brit. Pat. 9,728, July 3, 1915; *Chem. Abst.*, 1917, 95.

⁴⁸ Brit. Pat. 17,121, July 25, 1913; J.S.C.I., 1914, 1149; cf. U. S. Pat. 1,261,930, Apr. 9, 1918; *Chem. Abst.*, 1918, 1597.

⁴⁹ Brit. Pat. 103,720, Mar. 4, 1916; *Chem. Abst.*, 1917, 2042; cf. French Pat. 481,066, Feb. 25, 1916.

4933. In a paper by Hall on the cracking of oils read before "The Institution of Petroleum Technologists," 1914, the utility of steam as a source of hydrogen in cracking processes involving passing oil through heated tubes, is discussed by Hall, who states: "As far as any advantage from the use of water as a hydrogenating agent is concerned, I am sure it is nil, whether with or without a catalytic combiner, and I have operated fair-sized apparatus for weeks with nickel and other so-called catalyzers, first with and then without water, and we could never notice any material difference. If hydrogen without oxygen is utilized, better results are obtained, but the expense appears to be prohibitive. With nickel rods in the tubes, and with water used with the oil, I have found the rods so heavily coated after a six- or eight-hour run, that the coating could only be removed by buffing. It was impossible in any way to wipe it off. The substitution of copper for nickel rods gave equally good results. In large tubes, 1 in. or more, water in excess of 8 per cent or 10 per cent is utterly impracticable, if the process is conducted under pressure, and at any rate of feed that would be commercially economical, as no uniform pressures can be maintained."

4934. Hall further states that the admixture of water or steam with the oil during cracking neither prevents decomposition of carbon nor promotes hydrogenation of the unsaturated hydrocarbons. The latter, in large proportion, are objectionable in cracked spirit mainly because of the resinous carbon colloid with which they are usually associated and which, by oxidation, tends to form a varnish-like product detrimental to the working of motor engines. Owing to the combination effected in the compressor between the condensable vapor and the fixed gases, the spirit obtained by Hall's method is stated to be largely free from this objection.⁵⁰

4935. Testelin and Renard have proposed an apparatus for making volatile hydrocarbons from petroleum in the use of which the oil is passed under high pressure over refractory material such as clay which is maintained at a red heat. Steam is introduced with the oil.⁵¹

4936. Moeller and Wolterreck crack heavy oils by mixing their vapors with highly superheated steam at substantially atmospheric pressure and passing the mixture over coke at a dull red heat (600° to 800°). The sulphur present in the oil is at the same time converted into hydrogen sulphide and is thus removed from the oil. The steam is superheated to 700° to 800° in an apparatus which allows the steam to expand while it is being heated.⁵²

4937. In the treatment of hydrocarbons with superheated steam Hausmann and Pilat⁵³ recommend as catalyzers the oxides of iron, lead, cerium and manganese, also iron sulphate and calcium manganite. Lamplough⁵⁴ proposes to effect reaction between petroleum oil and water by passing a mixture of the vapors of these bodies over rods of metallic nickel while subjecting the vapors to a pressure and to a temperature approaching a dull red heat. From 20 to 60 parts of water are used to 100 parts of oil. Dibdin and Wolterreck⁵⁵ bring a mixture of superheated steam and petroleum oil into contact with iron, copper and other metals maintained at a bright orange heat to effect the simultaneous decomposition of the steam and hydrocarbon. They also mention (Brit. Pat. 26,666, 1905) the use of "proto-peroxide" of iron.

4938. Oil-shale Treatment. Vandergrift's process⁵⁶ consists in heating shale to volatilization temperature and then suddenly raising the temperature. The pyrobitumen is decomposed yielding hydrocarbons which have a lower density than those obtained at the vaporizing temperature. The steam from the natural moisture of the shale decomposes and the hydrogen hydrogenates the unsaturated hydrocarbons. The hydrocarbon vapors, before leaving the retort, are exposed to the catalytic action of a layer of incandescent spent shale; this takes up the excess of carbon. The final product has a high percentage of saturated hydrocarbons.

4938A. Shale is heated in a bath of molten metal in the presence of hydrogen, whereby fully-saturated petroleum products are obtained. The depth of the bath is such that the shale and gases are subjected to pressure, the maximum pressure being exerted at the bottom of the bath until the shale is decomposed. The spent materials are then released and allowed

⁵⁰ *J. Inst. Petrol. Tech.*, 1915, 1, 147; *J.S.C.I.*, 1916, 296.

⁵¹ U. S. Pat. 1,138,260, May 4, 1915; *Chem. Abst.*, 1915, 1689.

⁵² Brit. Pat. 16,611, July 19, 1913; *Chem. Abst.*, 1915, 148.

⁵³ Ger. Pat. 227,178, 1909.

⁵⁴ Brit. Pat. 19,702, 1912.

⁵⁵ Brit. Pat. 19,152, 1901.

⁵⁶ Can. Pat. 282,120, July 31, 1928, to The American Shale Reduction Co.; the apparatus is described in 282,110 of the same date; *Chem. Abst.*, 1928, 22, 3523.

to ascend quickly to the top of the bath; the resultant saturated hydrocarbon gases are collected and condensable constituents condensed.^{56a}

4938B. Light hydrocarbons are produced by the destructive hydrogenation of carbonaceous material which has been extracted from tar sands. The light oil or the middle oil from a previous hydrogenation forms a suitable solvent for the extraction, which is preferably carried out at temperatures above the normal. The middle oil produced may be separately treated, either by destructive hydrogenation or by cracking, to produce a further quantity of light oil.^{56a}

4938C. Popham^{56c} finds the presence of hydrogen advantageous when heating ground shale under pressure to obtain hydrocarbons of low boiling point.

4938D. Hydrogenation of shale oil^{56d} can be carried out at 280–290° and 75 atmospheres in the presence of a nickel catalyst, or by nascent hydrogen produced from zinc and acid; in either case the yield of solid paraffins is considerably increased.

4939. Lamplough⁵⁷ comments on the relative value of various catalysts employed in bringing about reaction between the vapors of oils and water. He states that burnt clay or aluminum silicate, which has frequently been recommended, is very slow in action and is open to the objection that the clay is apt to become clogged by deposition of tarry masses which can be removed only with great difficulty. The use of iron as a catalyzer is stated to be open to the objection that if the water vapor is used in excess the iron will rust and become unsuitable for use. Nickel in the form of fine particles is similar to clay with respect to becoming coated with particles of tarry or carbonaceous matter. On the other hand nickel in the form of a compact metal has been found by test to remain free of carbon deposits, while exhibiting the desired catalytic effect.

4940. Brooks⁵⁸ says that steam-iron processes for hydrogenating olefines and preventing deposition of carbon are inadequate.

DESULPHURIZATION

4941. Desulphurization by Hydrogenation. In a process for eliminating sulphur from oil, advanced by Evans, the oil is vaporized, mixed with 5 to 10 per cent of hydrogen, or with a gas containing hydrogen, and passed over a heated catalytic or contact substance such as nickel deposited on fire clay. Hydrogen sulphide is formed, and may be removed. If the oil cannot be distilled, it may be heated in contact with the catalyst while hydrogen is passed through or over it.⁵⁹

4942. The removal of sulphur from petroleum is effected, according to Schiller,⁶⁰ by generating hydrogen in a nascent condition in the oil during the distillation of the latter. It is claimed that sulphur is thus eliminated as hydrogen sulphide. Zinc dust and an alkaline hydrate, such as dry powdered caustic soda, are employed to generate hydrogen. These are added to the oil undergoing distillation. Huston⁶¹ proposes to remove sulphur by heating the vapors of a sulphur-containing petroleum oil admixed with steam to a temperature of 900° F. at which temperature it is said that the hydrogen of the water vapor unites with the sulphur, forming hydrogen sulphide. Hawes⁶² employs the same reaction and brings a mixture of vapor of hydrocarbon and water into contact with gravel contained in a chamber which is heated to a temperature of 400° to 600° F. Dubbs⁶³ forces a gas rich in hydrogen

^{56a} Jenson, U. S. Pat. 1,734,970, Nov. 12, 1929; *Brit. Chem. Abst.*, 1930, 48.

^{56b} Rule, Watts, and Imp. Chem. Ind., Ltd., Brit. Pat. 317,346, May 11, 1928; *Brit. Chem. Abst.*, 1929, 842B.

^{56c} *Ind. Chemist*, 1929, 5, 269–72; *Chem. Abst.*, 1929, 5035.

^{56d} Tanaka and Kobayashi, *J. Fuel Soc. Japan*, 1929, 8, 92–93; *Brit. Chem. Abst.*, 1929, 931B.

⁵⁷ U. S. Pat. 1,229,098, June 5, 1917.

⁵⁸ *J. Franklin Inst.*, 1915, 180, 653.

⁵⁹ Brit. Pat. 22,147, Nov. 6, 1914; *J.S.C.I.*, 1915, 2814.

⁶⁰ U. S. Pat. 580,652, Apr. 13, 1897.

⁶¹ U. S. Pat. 486,406, Nov. 15, 1892.

⁶² U. S. Pat. 444,833, Jan. 30, 1891.

⁶³ U. S. Pat. 470,911, Mar. 15, 1892.

through oil in a still to remove sulphur as hydrogen sulphide. Stevens ⁶⁴ claims steam reacts with the sulphur present in petroleum oils to form sulphurous acid, while the hydrogen thus liberated combines with the carbon of the oil, resulting in an increased yield of light oil. See also Turner ⁶⁵ and Noad. ⁶⁶ Hall ⁶⁷ uses "converting surfaces" of granite. Wilkinson ⁶⁸ has specified the distillation of petroleum oils with hydrogen.

4942A. Another process ^{68a} consists in treating oil with ammonia and with or without a catalyst. Hydrogen sulphide which is formed is removed by means of sodium plumbite or sodium stannate.

4943. Cracking and Hydrogenation at Atmospheric Pressure—Desulphurization. ⁶⁹ Tars, mineral oils, etc., after elimination of sulphur, are treated with water vapor or hydrogen-containing gas in the presence of *activated* hydrogenation catalysts at a temperature higher than that necessary for hydrogenation. Atmospheric or reduced pressure and temperatures of 250°–700° C. are suitable. The catalyst may be iron, nickel, cobalt, copper, zinc, or their oxides or salts, and the activating agent may be oxide of titanium, vanadium, chromium or manganese, or salts formed with the hydrogenation catalyst, e.g., copper chromate.

4943A. Elimination of sulphur is effected by passing over metal oxides or by treating with hydrogen-containing gases in the presence of activated hydrogenation catalysts formed from metals whose sulphides are readily reducible. Thus, a mixture of hydrogen and gas-oil vapor is desulphurized by passing over a heated catalyst obtained by reducing with hydrogen a mixture of copper oxide and chromic anhydride. The oil is washed with caustic soda and passed, with water-vapor, over nickel activated by alumina and potassium nitrite. The product is a low-boiling oil. ⁷⁰

4943B. Purification of Gas Containing Sulphuretted Hydrogen. ^{70a} Gases containing hydrogen sulphide, and preferably also ammonia, are purified by catalytic oxidation of the hydrogen sulphide, the catalyst consisting of a heavy metal, preferably one capable of combining with sulphur, to which has been added up to 10 per cent of an alkali or alkaline-earth salt, or of lead, bismuth, copper, or their compounds. One or more oxygen-transferring metals, group IV, V, or VI (e.g., chromium, vanadium), may also be added. The sulphur dioxide is recovered in the form of a sulphite-bisulphite mixture by treatment with a suitable alkaline agent.

4944. Hydrogenating and Desulphurizing Shale Oils. Bishop ⁷¹ treats oil-bearing materials (e.g., shale) with steam and carbon monoxide at 450°–500° C. The resulting nascent hydrogen reacts with sulphur present and hydrogenates unsaturated hydrocarbons. ⁷²

4945. Bourdelles ⁷³ has a process in which heavy hydrocarbons are vaporized or atomized with a large volume of steam and heated, at approximately atmospheric pressure, to between 350° and 450° C. in the presence of finely divided metals. This results in the desulphurization and hydrogenation of the hydrocarbons with the production of lighter oils. Regeneration of the metals can be effected *in situ*, by operation of valves, changing the composition of the gases.

4946. Liquid Hydrocarbons: Hydrogenation and Desulphurization. ⁷⁴ According to Mase, mixed steam and atomized oil are projected against a catalyst heated to 350°–450° C. Nascent hydrogen is produced and the oil is desulphurized and hydrogenated. The catalysts are iron, nickel, copper, cobalt, zinc, cadmium, vanadium, tungsten and carbon. By increasing the proportion of steam all the catalysts, except carbon, may be regenerated. ⁷⁵

4946A. The gases and vapors derived from the distillation of carbonaceous materials are passed successively through a purifier, a catalyst chamber, into which fresh hydrogenating

⁶⁴ U. S. Pat. 414,601, Nov. 5, 1889.

⁶⁵ U. S. Pat. 1,046,683, Dec. 10, 1912.

⁶⁶ U. S. Pat. 971,468, Sept. 27, 1910.

⁶⁷ U. S. Pat. 362,672, Nov. 8, 1887.

⁶⁸ U. S. Pat. 145,707, Dec. 16, 1873.

^{68a} French Pat., 575,598, April 24, 1924.

⁶⁹ I. G. Brit. Pat. 268,774, Mar. 30, 1927.

⁷⁰ *Chem. Age* (London), 1927, 16, 559.

^{70a} I. G. Farbenind. A.-G., Brit. Pat. 319,306, June 20, 1928; *Brit. Chem. Abst.*, 1929, 969B.

⁷¹ U. S. Pat. 1,610,242, Dec. 14, 1926.

⁷² *Chem. Abst.*, 1927, 491.

⁷³ French Pat. 632,378, July 23, 1926, to Bourdelles.

⁷⁴ Brit. Pat. 263,381, Apr. 4, 1926.

⁷⁵ *Brit. Chem. Abst.*, 1927, 180B.

gas is continuously introduced, and a second purifier. The first purifier, which may be charged with a metal or metal oxide maintained at about 400°, retains all the inorganic sulphur and the major portion of the organic sulphur; in the second purifier the enriched gases are freed from the hydrogen sulphide which is liberated by the constant regeneration of the catalyst. A part of the hydrogen set free in the second purifier may be returned to the cycle. If desired, the apparatus wherein the hydrocarbon vapors are condensed, or absorbed in wash oil or activated carbon, may be interposed between the catalyst chamber and the second purifier.^{75a}

4946B. French Pat. 673,333 ^{75b} describes a catalytic cracking process in which steam and hydrogen or other reducing gas is added to the hydrocarbon vapors to cause a constant reactivation of the catalyst by elimination of sulphur and oxygen.

4946C. Hydrocarbon fuels are obtained from the gaseous products of the distillation of carbonaceous material by passing the gas through purifiers to remove as much as possible of the organic and inorganic sulphur compounds, then over hydrogenation catalysts and finally through purifiers to remove sulphuric acid formed in the catalytic apparatus.^{75c}

4947. Hydrocarbons are obtained from mineral oils, tars, or their distillation products, by treating the initial materials preferably in the liquid state with hydrogen or gases capable of liberating it, and preferably in the presence of catalysts and at such temperatures and pressures that sulphurized and oxygenated compounds are eliminated, then submitting the products to cracking in the absence of hydrogen and with or without catalysts.⁷⁵

VARIOUS HYDROGENATIONS

4948. Franke claims that motor spirit is obtained from peat tar by distilling up to 320° and redistilling the distillate, preferably after it has been purified, up to 250°. The second distillation may be stopped at 170°, and the residue then heated up to 300° under pressure of 25 atmospheres in order to crack it. The cracking is accelerated by the addition of a catalytic agent capable of recombining with the oil the hydrogen which is evolved in the cracking: pyrophoric metals, such as iron, nickel, chromium and platinum are suitable for this purpose. The product of the first distillation is purified by treatment with oxidizing or condensing agents, preceded by the usual acid and alkali treatment. The oil is first treated with sulphuric acid, then washed and treated with a solution of caustic soda and again washed. Finally air is blown through the heated oil until it clarifies. Instead of oxidizing the residual phenolic compounds by treatment with air, manganese dioxide and sulphuric acid, or peroxides, persulphates, or chlorates, may be used, or condensing agents such as zinc or aluminum may be employed. The resinified phenolic compounds are removed by filtration before the second distillation.⁷⁷

4949. An apparatus for simultaneous ⁷⁸ cracking and hydrogenation is specified by the I. G. in two forms. In one the oil is fed on to the surface of a porous diaphragm through which the (presumably heated) hydrogenating gas passes from beneath the diaphragm up through the oil and its vapors. In the second form the oil is brought in below and around an electric heater which is surrounded by a porous jacket through which the hydrogen reaches the oil.⁷⁹

4950. A process vaguely reminiscent of that proposed by Brutzkus (para. 4700A) is described by Shore.⁸⁰ Oil such as crude petroleum is directed through the jacket of a compressor, then introduced together with hydrogen-bearing gases to a mechanically operating atomizer and the vapor produced is passed to the compressor cylinder and heated by compression; the highly heated vapor is then passed to expansion condensers.⁸¹

^{75a} Comp. Internat. pour la Fabr. des Essences et Pétroles, Brit. Pat. 302,683, Dec. 5, 1928; *Brit. Chem. Abst.*, 1930, 359B.

^{75b} Compagnie Internationale pour la Fabrication des Essences et Pétroles, July 30, 1928; *Chem. Abst.*, 1930, 2284.

^{75c} Compagnie Internationale pour la Fabrication des Essences et Pétroles, French Pat. 659,672, Dec. 20, 1927; *Chem. Abst.*, 1929, 5306.

⁷⁵ I. G. Farbenind. A.-G., French Pat. 659,583, Aug. 28, 1928; *Chem. Abst.*, 1929, 5312.

⁷⁷ Brit. Pat. 13,261, June 7, 1913.

⁷⁸ Brit. Pat. 272,539, June 11, 1926, by the I. G.

⁷⁹ *Chem. Age* (London), 1927, 17, 173.

⁸⁰ U. S. Pat. 1,687,595, Oct. 16, 1928.

⁸¹ *Chem. Abst.*, 1929, 23, 274.

4951. According to Rinker⁸³ the residue from the manufacture of oil gas may be treated directly with hydrogen to form new hydrocarbon compounds which are capable of further decomposition.

4952. Oil drops into a pressure vessel upon a porous surface of powdered glass, quartz, clay, etc., through which hydrogenating gases rise. The reaction vessel is lined with an alloy of 10 per cent chromium, 2 per cent molybdenum, 10 per cent cobalt, and 75 per cent iron.⁸⁴

4953. For the process described in the foregoing paragraph, horizontal rotating retorts with movable heating surfaces of nickel-chromium plates and containing balls of nickel-chromium are used.⁸⁴

4954. Oils are cracked by electrically heated bodies, which are submerged in the liquid and kept in motion therein. The process may be carried out in the presence of hydrogen or other gases, and under any convenient pressure. Any carbon which is formed becomes suspended in the liquid and is removed subsequently by filtration. The heating bodies and containing vessels are preferably constructed of materials which, in contact with the oil, do not become charged with electricity of opposite sign to that on the carbon particles.⁸⁵

4955. Cracking and Destructive Hydrogenation. Oils are cracked by heating them in a still by a heating device immersed in the liquid and exposed to intermittent or continuous blasts of gases supplied through a pipe. The heater is composed of a rod, spiral, or ribbon of metal or other conductive material, e.g., silicon carbide, graphite or charcoal, and is heated to at least 500° C. by electrical or other means. The gases may contain oxygen, hydrogen, or gases and vapor capable of giving off hydrogen but free from carbon. Brown coal tar pumped from a container and preheated in a vessel is passed through a pipe into the still which is heated externally to 350° C. The heater, consisting of a nickel-chromium ribbon, is raised to 750° C. by an electric current supplied through copper conductors and is treated with a blast of steam from the pipe. The vapors produced are condensed in a cooler while the gaseous products pass to a holder. Crude paraffin is treated in a similar manner.⁸⁶

4956. Van de Water and Sunderman describe a form of still for simultaneous cracking and hydrogenation of petroleum hydrocarbons.^{86a}

4956A. Hydrocarbons such as mineral oils, tars, etc., are converted into products of low boiling point by cracking with or without the addition of hydrogen and under such conditions that a carbonaceous precipitate is formed without formation of much gas, and treating the products still charged with the formed deposit, preferably in the liquid state, with hydrogen or gases yielding it immediately afterward at a high temperature and under high pressure with or without catalysts.^{86b}

4957. Apparatus and system for catalytic hydrogenation of liquid hydrocarbons or other reactions between gases and liquids are described by Steen.⁸⁷ The gas is introduced into the liquid in two streams, one of which imparts circulation to the liquid, while the other traverses the liquid in a direction opposite to that of the circulation. The process may be carried out under gradually increasing pressure by supplying gas at a rate greater than that of its absorption.⁸⁸

4958. Cracking and Hydrogenation with Simultaneously Produced Electrolytic Hydrogen. The Anderson apparatus⁸⁹ for cracking oils and hydrogenating the products embodies the following: a still, surmounted by a column; in each of these are nichrome coils which perform a quadruple function, (1) the nichrome acts as a catalyst, (2) the coils acts as electrodes, (3) the coils rotate as agitators, (4) the current passing through the coils produces heat. In the still is introduced a mixture of oil and water which is maintained at 315°-425° C. This heat and the electrolytic effect of the current decompose the water, producing hydrogen and oxygen. The hydrogen saturates the products of cracking while the oxygen combines with

⁸³ Can. Pat. 182,104, Feb. 5, 1918; *Chem. Abst.*, 1918, 763.

⁸⁴ Brit. Pat. 272,539, June 10, 1927.

⁸⁵ Brit. Pats. 272,194, May 23, 1927, 272,483 May 26, 1927.

⁸⁶ Brit. *Chem. Abst.*, 1928, 807B; Brit. Pat. 272,483, May 26, 1927, to I. G. Farbenind. A.-G.

^{86a} *Ill. Off. J.*, Oct. 17, 1928; Brit. Pat. 295,974, to I. G.

^{86b} U. S. Pat. 1,575,663, Mar. 9, 1926, assigned to Petroleum Labs., Inc.

⁸⁷ I. G. Farbenind. A.-G., French Pat. 659,906, Sept. 3, 1928; *Chem. Abst.*, 1929, 5312.

⁸⁸ Brit. Pat. 238,303, May 16, 1924.

⁸⁹ *Chem. Abst.*, 1926, 20, 2066.

⁹⁰ U. S. Pat. 1,599,629, Sept. 14, 1926.

the carbon formed. The reactions are completed in the column, where a temperature of 205°–315° C. is maintained. Natural gas may also be introduced to effect the hydrogenation.⁹⁰

4959. According to Carroll⁹¹ crude oil is distilled in a tubular boiler connected to a thermostatically controlled dephlegmator from which the products remaining liquid pass to a cracking apparatus. Cracking is carried out in an atmosphere rich in free hydrogen, and is effected by causing the oil to flow in thin layers over the surfaces of metallic baths arranged in the form of steps, successively larger or wider and raised to a sufficiently high temperature to cause the liquid to assume the spheroidal state, in order to obtain a superheating of the gaseous phase without corresponding superheating of the liquid phase.⁹²

4960. In apparatus for splitting oils or obtaining oil gas by igniting a mixture of hydrocarbons and hydrogen in a chamber, the valves controlling respectively the admission of the hydrocarbons through a pipe, the admission of hydrogen through a pipe, and the evacuation through pipes, of the carbon and gases produced, are interconnected so that the operation is repeated mechanically. The valves are opened by the rotation of cams fixed on a rotating rod, which also carries a cam which presses on a rod and thus operates a lever connected to the stem of the valve. The valves are normally held closed by springs. Correlation of the action of the sparking device is obtained by means of a cam.⁹³

4961. The following description mentions neither pressure nor any obvious catalyst. The *modus operandi* is not clear. Motor spirit is produced from petroleum or like hydrocarbons, hydrogen, and carbon monoxide by passing air and steam through incandescent coal, lignite, coke, or other solid fuel, conducting the mixed gases and undecomposed steam over scraps of tin plate, galvanized iron, copper-plated iron, or other two metals in close contact whereby further hydrogen is produced, and saturating the petroleum or other liquid hydrocarbon with the mixture. In practice the hot gases are led through a boiler to generate the steam, then through a still to crack the contained crude petroleum or paraffin oil, and finally into the receiver of the condensed distillate.⁹⁴ It would be easier to understand if the hot mixed gases first passed through the petroleum and carried it as vapor to be cracked and hydrogenated over the metal scrap, or if the petroleum vapor in some other fashion were brought over the metal scrap at a cracking temperature, simultaneously with the other gases.

4962. Heavy liquid hydrocarbons and hot hydrogen-containing gas are caused to flow in counter-current and in intimate contact under such conditions of temperature and pressure that chemical reaction takes place, the final products being lighter liquid hydrocarbons and a heavier gas containing gaseous hydrocarbons.⁹⁵

4962A. Converting Hydrocarbon Oils into Products of Lower Boiling Point.^{96a} In effecting conversion by use of a still adapted to contain a body of oil and having a plurality of compressors connected in series and located within the oil, a fixed hydrogen containing gas, such as that from a producer, and oil vapors are compressed in successive stages sufficiently to cause boiling of the oil in the still.

4962B. Destructive hydrogenation is carried out in a vertical pressure tower, the liquid being continuously agitated to give a thorough mixing with the hydrogen introduced at the base of the tower.^{96b}

4962C. In treating suspensions of coal, tars and mineral oils with hydrogen the material to be hydrogenated is kept in movement by means of dredgers, scrapers, paddles or the like. The gas is led in through a large number of small openings or nozzles under a pressure above that in the apparatus.^{96c}

4963. Ammonia in Hydrogenation of Cracked Oil.⁹⁶ V. L. Oil Processes, Ltd., and Lucas describe an apparatus and a procedure for cracking mineral oils in which a small quantity of

⁹⁰ Brit. Chem. Abst., 1926, 1004B.

⁹¹ Brit. Pat. 284,345, Jan. 28, 1928, to Carroll.

⁹² Brit. Chem. Abst., 1928, 919B.

⁹³ Brit. Pat. 295,938 to Fechter and Burger, Aug. 20, 1927; *Ill. Off. J.*, Oct. 17, 1928.

⁹⁴ Brit. Pat. 258,913, May 25, 1925, to Hirsch; *Univ. Oil Prod. Co. Libr. Bull.*, Dec. 18, 1926.

⁹⁵ U. S. Pat. 1,571,994 to Berry; *Brit. Chem. Abst.*, 1926, 352B.

^{96a} Danckwardt, U. S. Pat., 1,742,165, Dec. 31, 1929; *Chem. Abst.*, 1930, 1211; *Brit. Chem. Abst.*, 1930, 358B.

^{96b} Synthetic Ammonia & Nitrates, Ltd., French Pat. 668,064, Jan. 28, 1929; *Chem. Abst.*, 1930, 1499.

^{96c} I. G. Farbenind. A.-G., French Pat. 666,683, Oct. 30, 1928; *Chem. Abst.*, 1930, 1204.

⁹⁶ Brit. Pat. 244,875, Oct. 31, 1924.

ammonia gas is introduced into the cracking retort. This furnishes nascent hydrogen and thus aids in the production of saturated compounds. The description is, however, mainly concerned with the cracking retorts and the processes of cracking and recovery of products.

4964. A mixture of hydrocarbon material such as petroleum oil and hydrogen is forced through a conduit in which it is heated to about 540° under a maintained pressure of about 150 lb. per sq. in.; about 80–85 per cent of the mixture is vaporized and the resulting gases, vapors and liquid are drawn off and recovered.⁹⁷

4964A. A process described by Coultas ^{97a} consists in passing a hydrocarbon oil through a furnace having a series of coils of gradually increasing temperature until a temperature of 500° F. is reached. Hydrogen heated to about 1400° F. is then passed in and the resulting mixture is fractionated.

4964B. Apparatus for Hydrogenating and Cracking Oils from Shale.^{97b} A hydrogenator delivers directly to an "equilibrium chamber" below it, which has an outlet for lighter fractions through the hydrogenator and "equilibrium chamber" independent of the supply of fresh material.

4965. Hydrogenation in the Arc. Hirt subjects petroleum oil to an electric arc in the presence of hydrogen under pressure. Oxygen or steam may be introduced to remove carbon deposits.⁹⁸

4965A. Fester and Christen ^{98a} give data on the composition of the cracked gases, and of the distillation ranges of the cracked distillates obtained when mineral oil, through which a current of hydrogen is passed, and above the surface of which an electric arc is made to operate between electrodes formed of rods of either nickel or iron, is subjected to distillation.

4966. Leffer regards hydrogen as inert when used in his cracking process and, since he uses no catalyst and his pressures are moderate, the most that one could expect of molecular hydrogen is that it might somewhat depress dehydrogenation. In Leffer's process ⁹⁹ petroleum is distilled under pressure while an inert gas is circulating through the oil. Hydrogen is mentioned as an eligible inert gas.

4966A. Clark's Continuous Process.^{99a} A system of apparatus is described in which oil is heated under a pressure of at least 50 atmospheres in the presence of hydrogen; vapors and liquids produced are continuously withdrawn, and the liquids are continuously distilled in a plurality of distillation zones. Brit. Pat. 304,797 relates to a process in which a fraction is distilled from the oil under low pressure, the residual oil is hydrogenated under high pressure and the hydrogenated product is returned to the distillation zone.

4966B. Crude oil and bituminous material of not less than 20 per cent. volatile content are mixed in about equal proportions and heated at atmospheric pressure to 180° C. in a still provided with nickel or nickel plated stirrers. Low boiling constituents vaporize and are removed by condensation. The temperature is then raised to 320° C. and the pressure to 200 lb. per sq. in. and steam is admitted to assist the cracking and hydrogenation. Distillation is continued until the residue consists of a mixture of petroleum-pitch and coke, suitable for use as a fuel.^{99b}

4966C. Crude oils are cracked and the products are separated into light hydrocarbons and heavy hydrocarbons containing asphaltic products; the latter are then hydrogenated under a pressure of 50–200 atmospheres and at 750–950° F.

⁹⁷ U. S. Pat. 1,670,804, May 22, 1928, to Gomory, assigned to Leonard; *Chem. Abst.*, 1928, **22**, 2461.

^{97a} U. S. Pat. 1,628,532, May 10, 1927.

^{97b} Trumble, U. S. Pat. 1,725,320, Aug. 20, 1929; *Chem. Abst.*, **1929**, 4815.

⁹⁸ U. S. Pat. 1,250,879, Dec. 18, 1917.

^{98a} *Z. Elektrochem.*, **1930**, **36**, 17–20; *Brit. Chem. Abst.*, **1930**, 403B.

⁹⁹ Brit. Pat. 2328, 1912.

^{99a} Clark (to Standard Oil Development Co.), Brit. Pat. 304,796, Jan. 26, 1928; *Chem. Abst.*, **1929**, 4815.

^{99b} Cranston Brit. Pat. 322,167, Aug. 24, 1928.

and the gaseous products are separated while the liquid products are returned to the cracking stage. A preliminary hydrogenation may also precede the cracking of the oil.^{99c}

4966D. Hydrocarbons are obtained by treating carboniferous suspensions, tars, mineral oils, or their transformation products with hydrogen at high temperature and pressure, preferably in the presence of catalysts, in several steps, each step taking place under a pressure less than that of the preceding one.^{99d}

4966E. When high-boiling oils are hydrogenated at 1000 atmospheres and at a high temperature products of intermediate boiling point are obtained. At 200 atmospheres a larger proportion of light products is obtained, while at 20 atmospheres gas, light products, and carbonaceous residue without products of intermediate boiling point are obtained. Hydrogenation of suspensions of coal tar, etc., in stages is therefore advocated. The initial material is first hydrogenated in the liquid phase at 200–1000 atmospheres. The intermediate oils produced are then treated at 20–50 atmospheres in the gaseous phase whereby benzine is formed exothermically; catalysts may be used. Thus a crude oil (40–50 per cent boiling above 350° C.) is treated with hydrogen at 200 atmospheres and 450° C. in the presence of a chromium-molybdenum catalyst. Without any separation the product is expanded into a second chamber maintained at 20 atmospheres and 480° C. The mixture of gas and vapor obtained from the second chamber is cooled under pressure, and deposits a liquid consisting of benzine of high anti-knock value and about 25 per cent of kerosene (boiling point above 200° C.). Only a small proportion boils above 235° C., and there are no losses due to formation of gas and coke. Very heavy asphaltic oils are best treated in three stages at pressures of 1000, 200, and 20 atmospheres, respectively.^{99e}

4966F. Carbonaceous materials such as oils or coal suspensions are converted into hydrocarbons of low boiling point by intimate contact with hydrogen at high temperature and pressures in a reaction zone to which a portion of the treated material is returned after being withdrawn and reheated. Catalysts such as metal oxides are preferably used.^{99f} The reheating is effected in a coil through which the oil passes, preferably in admixture with both hydrogen and finely divided catalyst.

HYDROGENATION WITH SULPHIDES

4967. Hydrogenation with Hydrogen Sulphide.¹⁰⁰ Oils and tars are cracked under their own pressure; the resulting vapors are partially condensed. The lighter fractions are subjected to hydrogenation. This is effected by passing the vapors together with hydrogen sulphide, into a tower packed with a metallic mass. The sulphuretted hydrogen, reacting with the metal, liberates nascent hydrogen, which hydrogenates the cracked vapors. Two

^{99c} Haslam (to Standard Oil Development Co.), Brit. Pat. 314,871, July 3, 1928; *Chem. Abst.*, 1930, 1498.

^{99d} I. G. Farbenind. A.-G., French Pat. 659,584, Aug. 28, 1928; *Chem. Abst.*, 1929, 5312.

^{99e} I. G. Farbenind. A.-G., Brit. Pat. 296,431, Aug. 8, 1928; *Brit. Chem. Abst.*, 1929, 1041B.

^{99f} Haslam and Russell (to Standard Oil Development Co.), Brit. Pat. 304,301, Jan. 19, 1928; *Chem. Abst.*, 1929, 4802.

¹⁰⁰ Brit. Pat. 267,776, July 20, 1926, to Soc. luxembourgeoise des hydrocarbures, S. A.

towers operate alternately. The cycle starts with the passage of hydrogen-rich gases over the metal sulphide at a temperature which causes the reduction of the sulphide. The sulphuretted hydrogen thus produced is used as described. When the conversion of the metal to sulphide reaches the desired point, this tower is cut out of the hydrogenation circuit and used for the production of sulphuretted hydrogen as before.¹⁰¹

4968. To convert hydrocarbons of high boiling-points into products of low boiling-points, Rostin and Forwood suggest that a heavy hydrocarbon, in the form of vapor, be mixed with hydrogen sulphide and brought into contact with a substance such as heated copper capable of liberating the hydrogen of the hydrogen sulphide. The nascent hydrogen combines with the vapors of any unsaturated hydrocarbons produced. The copper sulphide arising from the operation may be treated with gases rich in hydrogen, forming hydrogen sulphide and copper.¹⁰²

4969. Oils from cracking, or destructive distillation, coal-gas, water-gas, or other liquid or gaseous hydrocarbon products are hydrogenated and purified by passage with hydrogen sulphide over iron which is, preferably, finely divided and freshly reduced. A temperature of 200°–300° C., is suitable for treating coal-gas or water-gas. When the iron is converted into sulphide the flow is stopped and hydrogen or gases containing hydrogen are passed through the material to re-form iron and hydrogen sulphide.¹⁰³

4970. According to Würth¹⁰⁴ a mixture of hydrogen sulphide and (a) the products obtained from a cracking process or (b) hydrocarbon vapors is subjected to a process in which nascent hydrogen is liberated by the thermal decomposition of the hydrogen sulphide.¹⁰⁵

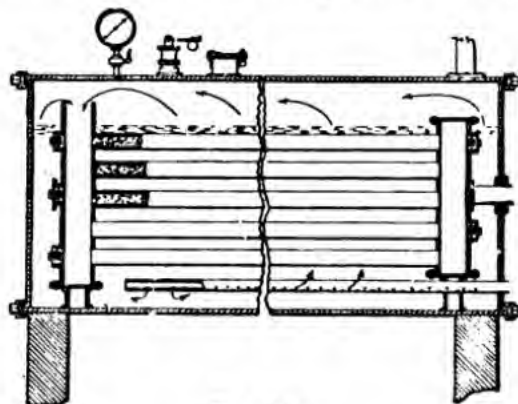


FIG. 114.

4971. The use of sulphur to promote the cracking of heavier oils to yield lighter products such as naphtha or benzine is suggested by Day.¹⁰⁶ He states that, by adding sulphur or a sulphur compound to crude oils or distillates containing little or no sulphur, such oils can be more easily decomposed by heat under the proper pressure with the production of an increased yield of distillates lighter in specific gravity than those which would be produced by the ordinary process of simple distillation. It is also stated that the distilling operation may be carried out in the presence of a hydrogen-containing gas and a catalytic agent or porous contact substance in the manner previously proposed by Day. The sulphur may be added to the oil in the form of the sulphide of ammonium, sodium, iron or copper or as hydrogen sulphide. Sulphates are not applicable for use in this process. A perforated supply pipe, see Fig. 114, for admitting oil and gas is placed near the bottom of the still. Hydrogen and

¹⁰¹ *Chem. Age* (London), 1927, **16**, 401. This closely resembles the process described in U. S. Pat. 1,451,052, Apr. 10, 1923, to Rostin, *Chem. Abst.*, 1923, **17**, 2048.

¹⁰² Brit. Pat. 107,034, May 15, 1916; cf. *Chem. Abst.*, **1918**, 1558; Dan. Pat. 22,824, Feb. 18, 1928. See also German Pat. 372,663, March 31, 1923, to Rostin.

¹⁰³ *Chem. Abst.*, 1929, **23**, 274; Brit. Pat. 286,255, Mar. 1, 1927, to Rostin. See also U. S. Pat. 1,732,111, Oct. 15, 1929; *Chem. Abst.*, **1930**, 234.

¹⁰⁴ French Pat. 622,715 (a) and 622,716 (b), Oct. 9, 1925, to Würth.

¹⁰⁵ Brit. *Chem. Abst.*, **1928**, 561B.

¹⁰⁶ U. S. Pat. 1,221,698, Apr. 3, 1917.

hydrogen sulphide may be admitted at this point. Contact material in the tubes above the perforated pipe may be iron "by hydrogen," zinc dust, reduced nickel or cobalt, dry porous clays, spongy platinum, or palladium. Day states he has found that the cracking operation is greatly aided by passing a hydrogen-carrying gas or vapor, such as hydrogen sulphide, ammonia, illuminating gas, or water-gas, or steam through the oil and thence passing the commingled oil vapors and hydrogen from the space above the oil through porous absorptive contact material. A catalytic action here takes place, the hydrogen being combined with the previously unsaturated hydrocarbons, resulting in the production of oils having a lower specific gravity and lower boiling-point.

4972. As examples of the carrying out of this process, Day states that he placed 100 cc. of crude petroleum in a retort, and first distilled off the distillate obtainable by the ordinary course of distillation obtaining on the average 3 per cent of distillate, distilling below 150° C., 20 per cent of distillate distilling between 150° and 300° C., in the case of Mexican oil from well No 4 of the Potrero del Llano district, Mexico, Province of Vera Cruz, and determined that the distillates, even the 3 per cent of naphtha distilling below 150°, had a burnt and objectionable odor and would be characterized by more than 50 per cent of unsaturated hydrocarbons. With another portion of the same crude oil, the distillation was repeated, using 5 to 10 per cent of sulphur. The result was an increase up to from 7 to 10 per cent in the yield of naphtha and up to 30 to 35 per cent of burning oil, the distillate between 150° and 300° C., having a very marked improvement in the odor, as soon as the sulphuretted hydrogen accompanying these distillates was removed by the addition of a dilute solution of soda. By the treatment of the first distillate obtained, without the addition of sulphur, with sulphuric acid it was impossible to obtain a water white oil; the distillate obtained with the use of sulphur was quite easily refined. Both samples were tested as to the content of unsaturated hydrocarbons, and it was found that the distillate between 150° and 300° C., by the ordinary process contained over 50 per cent of unsaturated hydrocarbons. The test was carried out by shaking the distillate for fifteen minutes with an equal volume of sulphuric acid of 1.84 gravity. This test when applied to the oil from the sulphur distillation, showed less than 20 per cent of unsaturated hydrocarbons. These experiments were carried out on a larger scale in iron stills in the laboratory of an oil-refining company with similar results.

4973. Rostin¹⁰⁷ heats mineral oils with hydrogen prepared by the passage of hydrogen sulphide over silver, which is preferably precipitated in a finely divided form on asbestos or pumice. The silver sulphide produced is readily reduced again by any gas mixture rich in hydrogen. Treatment of the oils with nascent hydrogen in this manner hydrogenates the unsaturated constituents, converting them into stable oils.¹⁰⁸

4974. French Pat. 633,127,¹⁰⁹ describes the hydrogenation of hydrocarbons, especially cracked products, whereby they are treated with hydrogen sulphide in presence of alloys of copper with aluminum, zinc, bismuth, or iron. These metals interact with the hydrogen sulphide, producing nascent hydrogen. When the metal has been converted into sulphide, it is regenerated by treatment with hydrogen, or gases containing hydrogen, at a higher temperature.

4975. Carbonaceous materials are treated with hydrogen or with gases containing or yielding hydrogen at high temperature and pressure in the presence of hydrogen sulphide or materials yielding hydrogen sulphide and molybdenum or tungsten, or both, or their compounds. Activators such as boric acid and chromium compounds may be added. The products obtained are almost entirely saturated aliphatic, aromatic and hydroaromatic hydrocarbons free from compounds of oxygen, sulphur and nitrogen and are stated to be sufficiently pure for use as motor fuels, lubricants, etc., without further treatment.¹¹⁰

4976. An apparatus for catalytic reactions and for regenerating catalysts is constructed so that hydrocarbon vapors are admitted to the catalyst through perforations or nozzles extending throughout the length of the boundary wall of the inlet passage surrounding or surrounded by the catalyst. The vapors may be treated with nascent hydrogen from injected hydrogen sulphide and metal oxide.¹¹¹

¹⁰⁷ French Pat. 603,101, July 10, 1925 to Rostin.

¹⁰⁸ *Brit. Chem. Abst.*, **1928**, 807B.

¹⁰⁹ To Rostin, Aug. 4, 1926; *Brit. Chem. Abst.*, **1930**, 359B.

¹¹⁰ Holzverkohlungs-Ind. A.-G., *Brit. Pat.* 313,505, June 12, 1928; *Chem. Abst.*, **1930**, 1204.

¹¹¹ *Brit. Pat.* 317,719, Aug. 20, 1928, to Comp. Internat. pour la Fabrication des Essences et Pétroles; *Chem. Abst.*, **1930**, 2015.

CHAPTER L

HYDROGENATION OF MINERAL OILS (III) INCLUDING LOW PRESSURE HYDROGENATIONS

OTHER CATALYTIC PROCESSES

5000. Day brought out a process in which he treated hydrocarbon oils with hydrogen in the presence of what he terms a porous absorptive substance, mentioning palladium-black, platinum sponge, zinc dust, fuller's earth and other clays. Figure 115 shows one method proposed by Day to this end. The upper chamber *A* is filled with hydrocarbon oil, and porous

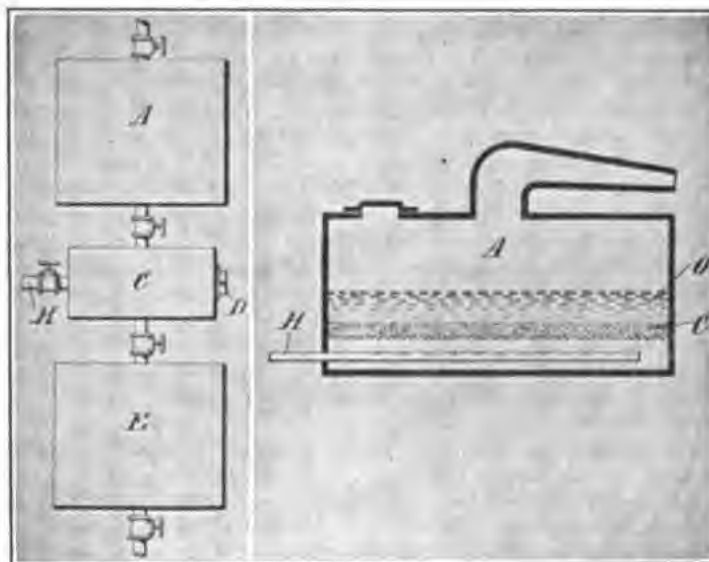


FIG. 115.

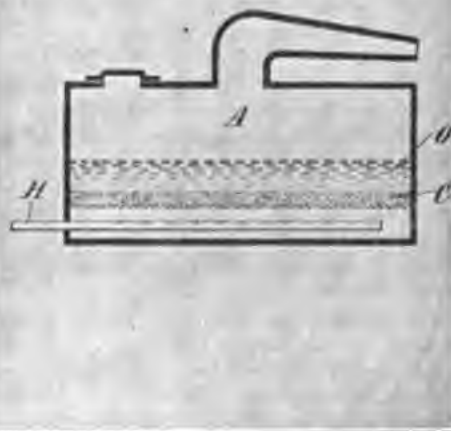


FIG. 116.

absorptive material, such as palladium-black, is introduced into the intermediate chamber *C* by way of the plugged orifice *D*. Any air present in *C* may be expelled by flushing out with hydrogen or an indifferent gas. Hydrogen is then admitted by the pipe *H* until the porous material has absorbed its full quota. The hydrogen gas may be admitted under a pressure of 100 lb. or more to the square inch. When the porous material in *C* has become properly charged with hydrogen, the oil is allowed to run from the chamber *A* through the chamber *C* into the collecting chamber *E*, hydrogen being introduced as required by the pipe *H*.

5001. In the place of hydrogen, Day states that ethylene or other hydrogen-carrying gas or vapor may be employed. By this treatment the disagreeable odor of hydrocarbon oils is in great part removed and the burning qualities of the oil improved. When palladium-black is used it is recommended that a proportion of one-half ounce to the gallon of oil be taken.

5002. Figure 116 shows a modification of Day's process. *A* is an oil still, in the lower part of which the perforated pipe *H* serves for the admission of hydrogen. Palladium-black or other porous absorptive material forms a layer *C*, on a screen above the hydrogen inlet. *O*

shows the charge of oil. In operating this apparatus the layer of material *C* is first charged with hydrogen and then oil run into the still. Distillation is carried out while hydrogen gas is being forced through the absorptive material and oil.¹

5003. Sabatier and Mailhe² recommend a two-stage method as follows: First stage: The vapors coming from solid or liquid hydrocarbons to be treated are directed against wires or metal blades rendered incandescent by an electric current. The liquid to be converted, or its vapor, is brought into contact with them either alone or mixed with hydrogen or any gas rich in hydrogen. Wires of various metals can be employed, either platinum or metal of the platinum series, iron, copper, cobalt, tantalum or any wires that can be rendered incandescent by an electric current of any kind, or wires covered with catalyzing metals or oxides, such as oxides of thorium, zirconium, uranium, titanous acid or mixtures of these oxides. The temperature of the wires is raised by the passage of electric current from 300° to dark or bright red. The dissociation of hydrocarbon products into more volatile hydrocarbon bodies is the more complete, the greater the length of contact of the wires, or the surface of the catalyzing metals, or catalyzing oxides heated by wires through which an electric current is passing. The output of volatile liquid products and of gas is the greater, the higher the temperature. At the outlet of the apparatus in which the kerosene or heavy petroleum oils have been exposed to the catalytic action, condensing apparatus is provided to cool the products of the reaction which comprise: 1. Hydrocarbon gases mixed with hydrogen, which can be utilized either directly for heating and lighting, or for explosion engines, or as compressed gases for lighting or for the manufacture of hydrogen by destructive distillation. 2. Liquid hydrocarbons distilling below 150°, containing non-saturated oxidizable hydrocarbons which are treated in the second stage. 3. Liquid hydrocarbons distilling between 150° and 300°, which can either be mixed again with the original raw material, in order to be submitted to a new treatment, or submitted to the action of the second stage in order to render them suitable for lighting purposes. 4. Liquid or solid products which do not distil under 300°, and which must be mixed again with the original raw material, in order to be submitted to a new treatment. 5. Solid carbon substances which are separated.

5004. Second stage: The liquids which are volatile under 150°, as well as those which distil between 150° and 300°, are constituted for the greater part of non-saturated oxidizable hydrocarbons, which can be utilized immediately for explosion engines, lighting, etc., or converted into saturated hydrocarbons which are practically non-oxidizable in the air, by direct hydrogenation of their vapors by means of divided nickel or similar metals. In order to carry out this second stage, hydrogenation may be effected by using, in place of divided nickel or similar metals, a nickel wire, blade or tube arranged in the form of a spiral or network, heated to a temperature between 200° and 350° C. by the passage of an electric current. Cobalt, copper, iron, platinum, or metals of the platinum series may be similarly employed. Divided nickel, copper, cobalt, iron, obtained by the reduction of their oxides; platinum in its various forms, or metals of the platinum group, supported on a metallic conductor also are recommended.

5005. Phillips and Bulteel³ claim to convert mineral oils into oils of lower specific gravity by heating with hydrogen in the presence of nickel or other catalytic agents. They state that the mixture of oil, gas and catalyst may be blown into a heated cylinder and the jet given a gyratory motion either by means of a nozzle revolving about its axis or by injecting the mixture tangentially to the periphery. In the latter case they state that the cylinder may have an axial core.

5006. Wallace⁴ describes a process and apparatus for the cracking and hydrogenation of mineral oil. The oil is introduced as spray or vapor into a horizontal or inclined chamber. Here it comes into contact with pieces of material (such as carbon, briquettes, firebrick, alumina) which may be coated with a catalyst (e.g., nickel). These fragments are in continuous motion in countercurrent to the gas and expose fresh surfaces of activity. Arrangements are described for return of the solid material to the cycle, with or without regeneration. The

¹ U. S. Pat. 826,089, July 17, 1906. Day took out U. S. Pat. 1,004,632, of Oct. 3, 1911, supplementing his earlier patent on the treatment of hydrocarbon oils with hydrogen. In the present instance tubes packed with catalyzer are placed in an oil still in such a manner that vapors from the oil may pass through the catalyzer tube in conjunction with hydrogen while being superheated by exterior contact of the tubes with boiling oil.

² U. S. Pat. 1,124,333, Jan. 12, 1915; *Chem. Abst.*, 1915, 710. French Pat. 475,303, Feb. 4, 1914; *J.S.C.I.*, 1916, 34.

³ Brit. Pat. 23,997, 1909.

⁴ Brit. Pat. 255,159, Apr. 17, 1925; *Brit. Chem. Abst.*, 1926, 779B.

hydrogenation is effected by the introduction of hydrogen, steam or producer gas. In an earlier patent ⁶ the same inventor claims to effect the hydrogenation or cracking by atomizing the oils (optionally with steam or hydrogenating gases) in proximity to a flame in the upper part of the reaction chamber which may be filled with refractory material (optionally treated with a catalyst). The materials pass downwardly through the refractory filling and cracking or hydrogenation may be effected either under increased or reduced pressure.⁶

5007. The hydrogenation of petroleum is carried out by Thompson in the following manner: A catalyzer is prepared by reducing the oxide, nitrate, carbonate, acetate or formate of nickel by hydrogen at a temperature of 320° to 350° C., for one-half to one hour. The catalyzer is added to the hydrocarbon which is heated in a cracking still and purified water-gas or pure hydrogen is passed through in large volume with strong pressure and agitation. The resulting mixture of gases and vapors is passed to condensers and the residual gases may be used again, if considerable hydrogen is present. As the above method of making the catalyzer gives a pyrophoric product, the reduced material should be mixed with oil and pumped to the still to avoid oxidation. Another method of preparing the catalyzer is to mix nickel formate with petroleum oil and pass the mixture into the still while injecting a strong current of water-gas. The passage of the gas through the oil serves to agitate the contents of the receptacle and the agitation may be further supplemented by a stirrer. Thompson states that the formate is decomposed, leaving the nickel in an almost colloidal state of fineness in the oil. An amount of catalyzer up to 2 per cent may be employed. The catalyzer is recovered from the still residue by washing with benzol.⁷

5008. A fuel suitable for use in automobile engines is obtained by Higgins and Preston ⁸ from heavy hydrocarbon oils by heating them in a converter under pressure to a temperature sufficient to volatilize the heaviest constituent of the oil, passing the vapors alone or with hydrogen gas over a catalyst, and condensing them in contact with the catalyst. The apparatus comprises a converter fitted with a pressure-regulating valve which is kept closed until the requisite temperature is reached. After the valve is opened, the vapors, together with hydrogen admitted into the converter, pass to a condenser which contains a cartridge of catalyst. The catalyst may consist of nickel oxide and pumice stone. The process may be applied to the treatment of shale oil, crude benzene, crude naphtha, crude tar oil, or paraffin oil, or to mixtures of crude benzene with crude naphtha, paraffin oil, or coal-tar oil.

5009. A process of making gasoline from heavier oils by cracking is described by Low.⁹ In one form of this process the oil to be cracked is sprayed into contact with a heating element which may carry a catalytic body. Iron, nickel, cobalt and copper are mentioned for this purpose. The spraying operation may be carried out in a closed vessel in an atmosphere of hydrogen or blue water-gas. Under such conditions it is stated that unsaturated compounds may be converted into saturated compounds. A hot nickel surface in a hydrogen-containing atmosphere is particularly advantageous in causing the formation of saturated gasoline from heavy oils projected against such surface.

5010. According to a process devised by Wells ¹⁰ directed to the production of gasoline from heavier petroleum products, oil vapors are conducted into a bath of molten lead, which is heated to about 480° to 540° C. and violently agitated by mechanical means at the moment of contact.¹¹

Wells ¹² also recommends the following cracking process: Preheated kerosene or a heavier petroleum oil is fed through a hot cracking chamber filled with jackstones coated with nickel or other catalyst and the crude gasoline thus formed is preferably refined by a further treatment with hydrogen and a catalyst at a temperature of about 240°.

5011. An apparatus for treating heavy oils and for hydrogenating the light oils produced has been devised by Brown.¹³ The apparatus is shown in Fig. 117, in which *a* is a still or boiler

⁶ Brit. Pat. 233,395, Feb. 1, 1924.

⁷ Chem. Abst., 1926, 20, 662.

⁸ U. S. Pat. 1,160,670, Nov. 16, 1915. In 1914 the Badische Co. recommended the hydrogenation of cracked petroleum residues at 100° C. and 80 atmospheres with the aid of a nickel catalyst carrying a promoter. See para. 636, example 7, page 59, this volume.

⁹ Brit. Pat. 23,876, Dec. 10, 1914; Chem. Abst., 1916, 1594.

¹⁰ U. S. Pat. 1,192,653, July 25, 1916.

¹¹ U. S. Pat. 1,187,874, June 20, 1916.

¹² J.S.C.I., 1916, 883.

¹³ U. S. Pat. 1,248,225, Nov. 27, 1917.

¹⁴ U. S. Pat. 1,225,569, May 8, 1917.

where the oil to be treated is placed. A pipe *b*, which extends to the bottom of the still, is used for the introduction of hydrogen. The vapor produced by heating the oil is mingled with hydrogen and passes through a vertical conduit in which are mounted perforated nickel plates *c*¹. These are supported by central rods *c*². In the upward passage of this vapor and hydrogen, contact with the surface of the nickel is brought about and it is claimed that the catalytic action of nickel is thus utilized. The volatile products obtained from the process are passed to a condenser. A water-cooling device *g* is placed about the conduit *c* in order to maintain the temperature sufficiently low to condense vapors of heavy oil, this condensate being returned to the still or boiler.

5012. Heavy oils, kerosenes and petroleum residues, are converted into gasoline and other volatile oils by distilling in a still in which hydrogen is injected into the oil by a pipe, and then passing the resulting mixture of oil vapor and hydrogen over nickel plates, the operation being effected under a pressure, e.g., 5 to 10 atmospheres. The nickel plates consist of perforated discs held in position in a vertical pipe by a central rod. The vertical pipe may also be lined with nickel. A cooling-system surrounding this pipe insures the return of heavy oils to the still.¹⁴

5013. Grené¹⁵ describes an apparatus in which heavy oils (e.g., those obtained in berginization or distillation of coal) may be cracked and hydrogenated by passing them, with neutral gases, through heated tubes containing superposed layers of (a) non-metallic porous catalyst such as activated charcoal, (b) oxide of manganese or of tin, (c) porous catalyst similar to (a) and, (d) a hydrogenating catalyst, such as nickel. Blast furnace gases containing oxides of carbon may serve as neutral gases. The hydrogen may be derived from decomposition of hydrogen sulphide formed from sulphur compounds in the oil, or may be derived by reaction of the oxides of carbon in the "neutral" gases with water vapor.¹⁶

5014. A process for improving the quality of hydrocarbon oils is described by the Badische Company. The oils are decolorized and deodorized by treatment in the fluid condition with hydrogen, at not above 200° C., at atmospheric or increased pressure, and in the presence of a catalyst, such as nickel, iron, cobalt or copper, or mixtures of these.¹⁷

5015. Trautmann's process (para. 4715) is applied to the cracking and hydrogenation of mineral oil.^{17a}

5016. Blümner's process¹⁸ is continuous. The liquid, mixed with a gas, e.g., hydrogen, is passed in a finely divided form through an externally heated bath of molten metal, and so brought into contact with catalysts contained as a finely divided filling or other suitable form in the melt. The process is especially suitable for bringing about chemical reactions between liquids and vapors or gases.¹⁹

5016A. In a process patented by Danckwardt^{19a} carbon or carbonaceous material is forced together with hydrogen under high pressure through a quantity of molten metal hydroxide which is being electrolyzed, using finely divided nickel as the cathode and an anode consisting of an electrical conductor through or near which fixed hydrocarbon gas is injected. The carbonaceous material is allowed to escape into another vessel where the

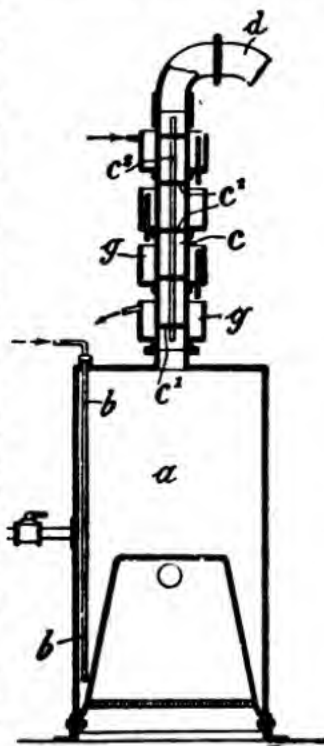


FIG. 117.

¹⁴ Dampierre, Brit. Pat. 109,796, Aug. 15, 1917; *Chem. Abst.*, 1918, 222. French Pat. 478,831, Feb. 22, 1915 and addition 20,331, Aug. 1, 1917; *Chem. Abst.*, 1916, 10, 2297 and 1918, 13, 1121.

¹⁵ Brit. Pat. 285,668, Mar. 21, 1927.

¹⁶ *Chem. Abst.*, 1929, 23, 274.

¹⁷ French Pat. 472,776, May 28, 1914; *J.S.C.I.*, 1915, 540.

^{17a} Brit. Pat. 261,786, Nov. 11, 1926.

¹⁸ Ger. Pat. 439,712, July 31, 1921; addition to Ger. Pat. 338,846.

¹⁹ Brit. *Chem. Abst.*, 1927, 695B.

^{19a} U. S. Pat. 1,730,997, Oct. 8, 1929; *Brit. Chem. Abst.*, 1929, 971B.

light hydrocarbons are separated from the heavier ones, the latter being returned with fixed carbonaceous material to the electrolyzer for re-treatment.

5017. Copper permutit catalyst characterizes a process which includes hydrogenation.²⁰ Crude mineral oil trickles down through a column lined with sheet cobalt and filled with the catalyst heated to 400° C. Hydrogen, or steam, is passed through in the same direction. The effluent vapor yields 20–30 per cent of liquid boiling up to 175° C., while the effluent liquid, which is 70–80 per cent of the total, is an oil boiling up to 200° C.²¹

5018. Electrolytic Iron as Hydrogenation Catalyst for Hydrocarbons. The characteristic feature of Tern's method²² is the use of iron prepared by electrolysis of iron salt solutions with platinum electrodes as a catalyst in the hydrogenation of petroleum residues, heavy tar oils and asphalt. These materials are subjected to a temperature of 250° C. and a hydrogen pressure of 20 atmospheres for six hours.

5019. A number of processes sponsored by Benzonaftene²³ deal with processes for successive catalytic treatments of heavy mineral and fatty oils for the production of liquids analogous to petroleum or naphtha. The processes, though interesting, need not be detailed here because they are not hydrogenations. One device, however, is described which is of interest, viz., a method²⁴ for making and for applying an adherent catalyst. The catalytic material (e.g., iron oxide, cerium oxide, copper, iron, nickel) is mixed into a paste with sodium silicate and applied to the inner surface of reaction chamber (retort).

5020. In a Prud'homme process²⁵ vapors of hydrocarbon fractions, boiling-point below 400° C., are treated above 180° C., with nickel oxide and copper oxide in succession to remove impurities, and are then passed with hydrogen, etc., first over a nickel catalyst and finally over active carbon. An oil distilling at 60°–220° C. is thus obtained.²⁶

5021. Cleaning of Catalyst in situ: Prud'homme Process.²⁷ In the hydrogenation of heavy hydrocarbons, crude petroleum or the like, after gasification and purification, vapors of a solvent are introduced continuously or from time to time into the catalyzer to remove deposits which tend to cover the catalyst. The solvent may be the first runnings from the fractional distillation of the hydrocarbons collected by condensation from the catalyzer.²⁸

5021A. Conversion of "Oil Tar" into Light Oils. Stephan²⁹ gives an account of the "Semo" (Prud'homme) catalytic process for obtaining from coal, etc., treated by any low-temperature carbonization process, the maximum yield of light oils suitable for motor or aviation spirit. The catalyst vessels contain tubes charged with specially treated finely divided nickel and cobalt, and through these the purified gas, to which has been added "mixed" gas, water-gas, and residual gas from the catalyst vessels, is rapidly passed; the reaction temperature must not be allowed to exceed 230°.

5022. Transformer Oils: Hydrogenation. Ferber²⁹ says that there is conclusive evidence that the deterioration of transformer oils with age is mainly due to the unsaturated compounds present. The practice has now been initiated of hydrogenating the oil to be used in transformers. The sulphur compounds are first removed by the usual acid and soda treatment followed by metallic sodium. The oil is then placed in an autoclave having either an agitator or a stirrer, and is heated with hydrogen at about 10 atmospheres pressure to 170°–200° C. (338°–392° F.) for two and one-half to three hours. A catalyst, preferably of nickel and copper, is used. A transformer oil hydrogenated in this way when exposed to the atmosphere at 120° C. (248° F.) for two hundred hours changed to a clear yellow color with faint blue fluorescence; no pitch or asphalt formed.³⁰

²⁰ Brit. Pat. 271,451, May 20, 1926, by the I. G.

²¹ *Chem. Age* (London), 1927, 17, 115.

²² Ger. Pat. 336,334, Dec. 24, 1918; *J.S.C.I.*, 1921, 40, 651A.

²³ Brit. Pat. applications by Benzonaftene, 231,157, Mar. 24, 1924; 231,458, convention date Mar. 26, 1924; 231,459, same date; 231,460, same date; 231,461, convention date, Mar. 28, 1924.

²⁴ See 231,458 and 231,459.

²⁵ U. S. Pat. 1,674,796, June 26, 1928, to Prud'homme, assigned to Soc. internat. proc. Prud'homme.

²⁶ *Brit. Chem. Abst.*, 1928, 779B.

²⁷ French Pat. 637,022, Oct. 26, 1926, to Prud'homme (assigned to Soc. internat. proc. Prud'homme).

²⁸ *Chem. Abst.*, 1929, 23, 698.

²⁹ *Colliery Guardian*, 1929, Dec. 6; *Gas J.*, 1930, 189, 92–93; *Brit. Chem. Abst.*, 1930, 173B.

³⁰ *Die Metallbörse*, Oct. 17, 1928, 2301. *Petrol. Times*, 1928, 898.

³¹ *Univ. Oil Prod. Co. Bulletin*.

5022A. Crude paraffin wax is treated at a temperature of 300°–400° C. and pressure of 10–250 atmospheres with hydrogen or gases containing it, the conditions being such that little or no cracking takes place. A catalyst may be employed consisting of one or more oxides of the metals of groups 3, 4, or 6, together with iron, nickel, or cobalt, or their oxides as activators. Suitable catalysts include molybdic acid, mixtures of molybdenum trioxide, or dioxide with alumina, nickel oxide, zirconium oxide, chromic oxide, silica gel, or cerium oxide, or a mixture of aluminum and chromic oxides, or a mixture of zirconium oxide and chromic acid.^{30a}

5023. Refining Mineral Oil by Hydrogenation. According to Bullinger³¹ mineral oils are treated with hydrogen at 10 atmospheres and 150°–300° C. in presence of nickel, deposited on an inert carrier, with or without cobalt, iron or copper.

5024. In Clancy's method³² petroleum (crude or other) with hydrogen is led over a molten body containing sodium cyanide, then through a cracking retort filled with nickel packing.

5024A. Low boiling point oils are obtained from those of higher boiling point by distillation in contact with sodium cyanide or other suitable cyanide or cyanate in molten form. Hydrogenation of the vapors is effected by ammonia formed during the reaction; ammonia and other hydrogenating gases may also be admitted from an extraneous source. Metallic catalysts such as iron, nickel or copper may be added. The cyanide is regenerated by heating it with the carbonaceous residues and an alkali carbonate, hydroxide or formate in the presence of nitrogenous gases.^{32a}

5024B. Mineral oils, tars, and their hydrogenation products are converted into hydrocarbons of low boiling point by subjecting them at 410–600° and in the presence of gases or vapors and of suitable catalysts, to the action of aldehydes or ketones which contain more than three atoms of carbon in the molecule.^{32b}

5024C. Mineral oils, tars, and hydrogenation products of these substances and of coal are distilled at 410–600°, under pressure, in the presence of amides, amines, with or without aldehydes or ketones which contain more than 3 atoms of carbon in the molecule; cracking is facilitated by the admixture of metals and their compounds capable of combining with aldehydes and ketones. A tar fraction, boiling point 200°, which was cracked at 600° with 2 per cent of formamide, in a quartz column filled with pumice, yielded 31 per cent of products boiling below 200°. ^{32c}

5024D. Cracking Hydrocarbons.^{32d} Mineral oils, tars, coal hydrogenation products, etc., are converted to hydrocarbons of low boiling point by heating them with compounds or mixtures of organic acids or substances yielding them and inorganic salts, preferably under pressure and in the presence of hydrogen.

5025. The *Scientific American*³³ observes that an English company is securing a very large yield of gasoline from petroleum by catalytic hydrogenation. A tall still with a conical bottom receives a steady feed of petroleum and hydrogen gas under pressure. This mixture enters at the bottom and passes over finely divided nickel which catalytically brings about a reaction between the hydrogen and oil. Gasoline is formed which passes off as a vapor at the temperature of the still, while the heavier hydrocarbons formed fall back into the catalyst and react with hydrogen. Finally a tarry residue must be removed and the nickel regenerated. The issuing gases pass into a cooling chamber where the gasoline is condensed. The hydrogen unused up to that point is forced back and passed through the still once more.

5026. Hydrogenating Hydrocarbons, etc. Ferric Chloride and Aluminum Chloride Catalysts. Kling and Florentin³⁴ state that light hydrocarbons are obtained from heavy or cyclic hydrocarbons by heating with hydrogen under pressure in the presence of a catalyst

^{30a} I. G. Farbenind. A.-G., Brit. Pat. 320,921, July 19, 1928; *Chem. Age* (London), **1929**, 628.

³¹ Brit. Pat. 218,989, July 14, 1923, to Bullinger, *et al.*

³² U. S. Pat. 1,658,116, Feb. 7, 1928.

^{32a} Clancy, Brit. Pat. 304,421, Nov. 21, 1927; *Chem. Abst.*, **1929**, 4815.

^{32b} I. G. Farbenind. A.-G., Brit. Pat. 315,991, July 7, 1928; *Brit. Chem. Abst.*, **1929**, 843B; *Chem. Abst.*, **1930**, 1735.

^{32c} I. G. Farbenind. A.-G., Brit. Pat. 320,421, July 7, 1928; *Brit. Chem. Abst.*, **1929**, 1006B.

^{32d} I. G. Farbenind. A.-G., French Pat. 660,559, Sept. 18, 1928; *Chem. Abst.*, **1930**, 234.

³³ May 23, 1914.

³⁴ Brit. Pat. 253,507, June 12, 1925, to Kling and Florentin.

furnishing addition or substitution products splitting at lower temperatures, e.g., at temperatures of 350°–460° C., without formation of coke or tar. Carbon monoxide or hydrocarbon gas may be mixed with the hydrogen and chlorides or other halides of the alkaline earth metals and earth metals or "nitrated, hydroxylated, and like derivatives" may be used as catalysts, for the hydrogenation of naphthalene, anthracene, cyclohexane and their derivatives, heavy tar oils, pitch, coal, colophony, asphalt and petroleum distillation residues. A mixture of ferric and aluminum chlorides may be used in hydrogenating naphthalene to obtain a light oil distilling mostly at 100°–200° C.³⁵

5027. Hydrogenation with Aluminum Chloride Catalyst. The hydrogen content of asphaltic petroleum oils is increased by heating with gas rich in hydrogen in the presence of aluminum chloride until the asphalt has practically disappeared.³⁶

5028. Cracked gasoline is improved by warming it with anhydrous aluminum chloride (without the possibility of distillation) and supplying gases rich in hydrogen to the reacting mixture.³⁷

5028A. Hofmann and Wulff^{37a} describe a process which is carried out in the presence of a halide of boron or of an addition product thereof, e.g., $(C_2H_5)_2O \cdot BF_3$. In the presence of such a catalyst only small amounts of gases such as methane or of carbon deposits are produced. Owing to the catalysts being gases or liquids, a good distribution of them throughout the material is obtained. A crude mineral oil, boiling above 300°, in the presence of the catalyst (5 per cent) and hydrogen at 150 atmospheres and 380° gave a 75 per cent yield of oil boiling below 250° and 15 per cent of a highly viscous lubricating oil. With the double compound (10 per cent) at 400° and 1 atmosphere a yield of 60 per cent of light oil was obtained.

5029. Sludging of Mineral Oils Prevented by Hydrogenation. Oil is made non-sludging by treating it with nascent hydrogen at a temperature so low that cracking does not take place. The sludge-forming constituents are reduced to compounds which do not produce sludge.³⁸

5030. Moody³⁹ also describes a method of accomplishing the hydrogenation mentioned in the last paragraph. This consists in treating the oil with aluminum chloride (or salt having a similar action) and aluminum carbide (or other carbide which will cause the evolution of hydrogen by interaction with the salt) at 120°–150° C. Higher temperatures cut down the reaction time, which at the temperatures mentioned is from two to five hours. A satisfactory proportion of salt and carbide is 5 per cent of each. The reagents should be intimately mixed with the oil. Preliminary purification with bone charcoal, fuller's earth, or similar clarifying agent is sometimes desirable. Molecular hydrogen may be introduced during the reaction to supplement the hydrogenation of the unsaturated bodies.

5031. Treatment of Aluminum Chloride Sludges. In order to produce low-boiling oils from the chloride sludges formed by distilling high-boiling oils with aluminum chloride, the sludges are mingled with a molten mixture of sodium and zinc chlorides in the presence of hydrogen while the molten mixture is circulated through a mass of nickel packing units, of which at least part are held at cracking temperature.⁴⁰

5032. Recovery of Metallic Halides from Hydrocarbon Sludges. The sludge produced during the conversion of hydrocarbons in the presence of halides is subjected to simultaneous cracking and hydrogenation, whereby lighter saturated hydrocarbons are formed and the halide is liberated for further use.⁴¹

5033. Treating Crude Petroleum and Other Hydrocarbons to Increase the Yield of Lighter Products. The yield of gasoline from a crude petroleum is increased by adding gasoline, distilling under a pressure of 10 atmospheres and a temperature of 100°–300° C., and subjecting the vapors to the action of a hydrogenating catalyst.⁴²

5034. Melamid Process for Oils. In the application of the Melamid process to mineral oil,⁴³ the oil to be cracked is introduced in an atomized condition, together with hydrogen,

³⁵ *Chem. Abstr.*, 1927, **21**, 2556; *Cf.* French Pat. 607,155, June 6, 1925.

³⁶ U. S. Pat. (to McAfee) 1,608,328, Nov. 23, 1926.

³⁷ U. S. Pat. (to McAfee) 1,608,329, Nov. 23, 1926.

^{37a} Brit. Pat. 301,395, Nov. 27, 1928; *Brit. Chem. Abstr.*, 1930, 134B.

³⁸ U. S. Pat. 1,472,882, Nov. 6, 1923, to Moody.

³⁹ U. S. Pat. 1,601,406, Sept. 28, 1926.

⁴⁰ U. S. Pat. 1,620,075, Mar. 8, 1927, to Clancy.

⁴¹ U. S. Pat. 1,582,131, Apr. 27, 1926, to Danner, assignor to Standard Oil Co.

⁴² Brit. Pat. 206,121, Nov. 14, 1923, to Gane.

⁴³ Brit. Pat. 231,190, Mar. 20, 1925. U. S. Pat. 1,723,431, Aug. 6, 1929; *Brit. Chem. Abstr.*, 1929, 932B. *Cf.* para. 4714.

into the reaction vessel, which contains a liquid contact substance such as molten tin at 300°–400° C. (*cf.* Brit. Pat. 221,559). The temperature is so adjusted that the oils of lower boiling-point are cracked, while the fractions of higher boiling-point are withdrawn unchanged from the reaction vessel, thereby avoiding coke formation.⁴⁴

5035. In another Melamid process the tar, mineral oil, etc., is dispersed in a mist with hydrogen and treated at a high temperature (e.g., 500° C. for crude petroleum) in presence of a catalyst which liquefies at that temperature and which does not form carbides.⁴⁵

5036. Olefines and Diolefines. Olefines and diolefines are obtained by catalytic treatment in a vaporous state of paraffins, olefines or their mixtures at temperatures between 500–800° C., using as catalyst lustrous carbon (glanzkohle) which is deposited from hydrocarbons at temperatures above 650°. It may advantageously be employed on carriers, such as difficultly reducible metal oxides, e.g., glucinum oxide, tricalcium phosphate, alumina, chromic oxide, active silica, natural or artificial silicates, quartz, porcelain or on metals, like copper or chromium. Suitable starting materials comprise cyclohexane, tetrahydrobenzene, tetrahydronaphthalene, terpenes, naphthenes, Caucasian naphthas, crude mineral oils, conversion and cracking products thereof, products of the hydrogenation of carbonaceous substances, benzenes, tars containing paraffines, or mixtures of the above. The process may be carried out at ordinary or reduced pressures, and preferably in the presence of diluents, comprising gases and vapors, which do not react with the substances taking part at the temperature of reaction, such as water vapor, nitrogen, carbon dioxide, methane, etc. Further treatment of the reaction product may consist in fractional distillation under pressure.⁴⁶

5037. Purification of Cracked Spirit. Remfry treats vapors of cracked petroleum, at a temperature 10°–20° C. above the final boiling-point, with dense, porous, activated charcoal. This produces a sweet, non-gumming (non-polymerizing) product. The treatment may be carried out in presence of hydrogen, but this is not essential.⁴⁷

5037A. Crude material is treated with 2 to 3 per cent of a concentrated solution of hydrogen chloride in ethyl or methyl alcohol, or other organic solvent, after a pretreatment, if desired, with gaseous or aqueous hydrogen chloride. The heavier oils are preferably diluted with benzine before treatment.⁴⁸

5037B. Hofmann and Wulff⁴⁹ also suggest refining oils by washing them with a solution of sulphuric or phosphoric acid dissolved in alcohol.

5037C. Oils obtained by the hydrogenation of coal, or cracking of mineral oils, are freed from solid substances by adding solvents for the oil, with or without wetting agents such as aromatic sulphonic acids, and centrifuging.⁴⁶

5037D. Solid and liquid products from the destructive hydrogenation of carbonaceous materials are separated by adding an insoluble finely divided carbonaceous material and then filtering. An oil capable of dissolving pitch may be added before filtration. The residue on filtering forms a fuel. French Pat. 666,873 describes the addition of an oil of relatively high boiling point coming from the hydrogenation process itself. The resulting liquid is submitted to a further destructive hydrogenation.⁴⁶

5038. Purification of Oxidation Products by Hydrogenation. Hydrogenation over nickel catalyst in the liquid phase at high pressures (150 to 1000 lb.) and at temperatures of 100°–200° C., is claimed by James⁴⁷ as a method for purifying and improving the products of the partial oxidation of hydrocarbons. The oxidation products contain unsaturated bodies, bodies of aldehydic character and so on, which are objectionable because they possess peculiar odors, and some of them tend to resinify. As the material contains catalyst poison, it is subjected to a preliminary treatment with the catalyst (probably spent catalyst could be used in practice).⁴⁸ James does not confine himself to molecular hydrogen, but mentions methods of producing hydrogen in presence of the bodies to be hydrogenated.⁴⁹

⁴⁴ *Chem. & Ind.*, Aug. 6, 1926. According to Ger. Pat. 415,371, of April 26, 1923, to Melamid, the vessels for hydrogenation are made of or lined with graphite.

⁴⁵ *Chem. Abst.*, 1927, 20, 3800; U. S. Pat. 1,602,310, to Melamid.

⁴⁶ Brit. Pat. 303,998, Dec. 14, 1927 to Johnson (from I. G.); *Illus. Off. J.*, 1929, 412.

⁴⁷ Brit. Pat. 205,868, July 22, 1922.

⁴⁸ Hofmann and Wulff, Brit. Pat. 298,484, Oct. 8, 1928; *Brit. Chem. Abst.*, 1930, 406B.

⁴⁹ Brit. Pat. 301,420, Nov. 1, 1928; *Brit. Chem. Abst.*, 1930, 450B.

⁴⁶ I. G. Farbenind. A.-G., French Pat. 662,387, Oct. 16, 1928; *Chem. Abst.*, 1930, 491.

⁴⁶ Imp. Chem. Ind., Ltd., French Pat. 666,872, Dec. 31, 1928; *Chem. Abst.*, 1930, 1204.

⁴⁷ U. S. Pat. 1,681,238, Aug. 21, 1928.

⁴⁸ See Ellis, para. 548.

⁴⁹ The same patent mentions other methods of purification such as halogen addition or mild oxygenation.

5038A. A method of refining hydrogenation products is to extract the material with a reagent having a high partial pressure of ammonia, whereby oxygenated impurities are removed. Suitable extracting reagents are liquid ammonia or a solution of ammonia in methanol.^{49a}

5038B. A non-knocking motor fuel having a final boiling point of 185° is obtained by mixing a knocking gasoline boiling below 150°, with an anti-knocking hydrocarbon fraction of boiling range 150 to 180°, which may be obtained by (a) distilling aromatic tars or aromatic petroleum; (b) condensation of unsaturated compounds; (c) destructive hydrogenation or dehydrogenation of aliphatic or hydroaromatic compounds, aromatic middle oils, such as anthracene oils, coal-tar products, residues obtained by cracking and high-temperature tars; or (d) by the extraction of products of appropriate boiling range with sulphur dioxide.^{49b}

5038C. Coal tars and mineral oils are treated with solutions to separate them into fractions rich in hydrogen and fractions poor in hydrogen. The former may be used as they are, or after treatment with hydrogen, as lighting or Diesel oils, and the latter are treated with hydrogen under pressure to obtain motor oils. The solvent may be sulphurous acid.^{49c}

5039. Hydrogenation and Oxidation of Mineral Oil [and product for use as paint vehicle, etc.]. Blakeman's method is applied specially to asphaltic oil of the Texas type. Hydrogenation preferably precedes oxidation.⁵⁰

5039A. Alkyl Halides, Glycols, and Alcohols from Cracked Gases.^{50a} The constituents of the gas are fractionated by liquefaction and the monochlorhydrins formed. These are hydrogenated in the presence of powdered nickel, cobalt, or copper to obtain the corresponding alkyl halide, which on hydrolysis yields the alcohol. Direct hydrolysis of the chlorhydrins yields the corresponding glycols.

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- 5042.** Dunstan. Scientific foundations of the refining of petroleum. V. Cracking, *J. Roy. Soc. Arts*, 1928, 76, 1001. A lecture touching briefly on berginization.
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- 5043A.** Ormandy. *J. Inst. Fuel*, 1929, **2**, 199-204; *Chem. Abst.*, 1929, 4562. Liquid fuels. A discussion including hydrogenation and catalytic processes.
- 5044.** Ramage. Cracking with hydrogenation, developments in England (news note). *Chem. Age* (London), 1928, **19**, 540.
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- 5046.** Sedlaczek. Development of cracking processes as shown in German patents. *Erdöl u. Teer*, Mar. 11 and 18, 1926. A review of a large number of German patents, some of which use hydrogenation.

^{49a} I. G. Farbenind. A.-G., Ger. Pat. 489,346, Jan. 1, 1926, Pier and Eisenhut, inventors; *Chem. Abst.*, 1930, 2275.

^{49b} I. G. Farbenind. A.-G., Brit. Pat. 325,858, Aug. 29, 1928; *Brit. Chem. Abst.*, 1930, 451B.

^{49c} I. G. Farbenind. A.-G., French Pat. 673,824, April 22, 1929; *Chem. Abst.*, 1930, 2580.

⁵⁰ U. S. Pat. 1,385,037, 1921; also U. S. Pat. 1,385,035, to same patentee for admixture of product with tung oil; U. S. Pat. 1,385,034 same, plus anhydrous pigment.

^{50a} Soc. Anon. d'Explosifs et de Prod. Chim. (Addn. 32,638, April 13, 1926, to French Pat. 610,434); *Brit. Chem. Abst.*, 1930, 232.

5047. Steinkopt and Beirsdorf, Catalytic Hydrogenation of Laevo-rotatory Java Oil Fractions. *J. prakt. Chem.*, 1920, **101**, 75. No change in optical properties, therefore *l*-rotation not due to cholesterylene.

5048. Wagner. The hydrogenation of cracked gasoline, results of some experiments, *Nat. Petr. News*, April 14, 1926, 86. Gasoline hydrogenated by Sabatier's method. Comparison of sulphuric acid absorption, iodine number and oxygen absorption (permanganate).

5049. Waterman and Perquin. Hydrogenation in the petroleum industry. *J. Inst. Petrol. Tech.*, 1925, **11**, 36. Chiefly an account of Waterman and Perquin's own work already described in the section of this book on berginization.

5050. Zelinski and Lavroski. Oleic, palmitic and stearic acids as mother substances of petroleum. *Ber.*, 1928, **61B**, 1054; *Chem. Abst.*, 1928, **22**, 2920 (a full abstract). Heated with aluminum chlorides the fatty acids gave hydrocarbons, those from oleic were highly unsaturated, the others chiefly paraffins. Hydrogenation was used in the investigation of the unsaturated hydrocarbons.

5051. Beeswax heated with 30 per cent of aluminum chloride began to decompose at 120° and yielded 80 per cent of liquid and solid products from which was isolated a substance volatile with steam, boiling range 70–300°, consisting chiefly of paraffin hydrocarbons. Hydrocarbons volatile with steam, boiling range 90–210°, on hydrogenation with platinum-charcoal gave a light naphtha oil in which cycloparaffin hydrocarbons predominated. Zelinski and Lavrovski, *Ber.*, 1929, **62B**, 1264–6; *Chem. Abst.*, 1929, 4667.

5052. A high-pressure conducting tube with an adjustable cross-section, for use in the hydrogenation of carbon and mineral oils, is described in German Pat. 490,562 to Deutsche Bergin-A.-G. für Kohle und Erdölchemie, Noack inventor, Sept. 22, 1926; *Chem. Abst.*, 1930, 2274.

5053. Device for separating products of destructive hydrogenation or other liquids and gases under pressure. Harrison and Imperial Chemical Industries, Ltd., Brit. Pat. 310,985, Dec. 31, 1927; *Chem. Abst.*, 1930, 670.

5054. Stable emulsions containing mineral oil products and aqueous aliphatic alcohols are prepared by treating mixtures of these substances with nascent hydrogen at a raised temperature. Thus, a mixture of the components containing a small quantity of an organic acid, e.g., oxalic acid, may be led through a granulated lead-nickel alloy, or a mixture containing a small quantity of a volatile inorganic acid, e.g., hydrochloric acid, may be led in the vapor state over granulated zinc. The emulsions are useful as fuel. Kirschner, German Patent 482,931, Sept. 10, 1926; *Chem. Abst.*, 1930, 497.

CHAPTER LI

ELECTRICAL METHODS OF HYDROGENATING FATTY AND MINERAL OILS

5100. Reference has been made to the work of De Hemptinne on the effect of electrical discharge in causing the addition of hydrogen to unsaturated oils. Later work by this investigator ¹ furnishes additional data on this interesting reaction. The formation of stearine by the action of an electric discharge on commercial olein in an atmosphere of hydrogen was studied on both a small and large scale. The apparatus employed on a large scale consists of a rotatable horizontal axle bearing a large number of thin, parallel, vertical iron plates separated by glass plates, the former being connected together alternately on opposite sides. The whole is mounted in an air-tight iron drum which is partially filled with olein and into which hydrogen is introduced; the odd numbers of the iron plates are connected with one pole of a high-potential alternator and the even numbers with the other pole. When the axle is rotated, the electric discharge passes through a thin layer of olein which constantly wets the plates. The glass dielectric may be arranged so as to contact with one or both faces of the iron plates (the free space in the latter case being between the dielectrics) or the dielectrics may be separated from both faces of the iron plates. The capacity of the largest apparatus constructed was about 1000 lb. Apart from the construction of the apparatus the yield is influenced by the current density, the frequency of the current, gaseous pressure, temperature of the liquid and the distance between consecutive iron plates. If the reduction is not pushed beyond a point corresponding to a 15 per cent decrease in the iodine number, there is a complete parallelism between the decrease in the iodine number, increase of melting-point and absorption of hydrogen. The variation of the iodine number or the increase of the melting-point per unit of electrical energy employed is taken as a measure of the transformation effected. A proportionality between the quantity of substance transformed and the intensity of current does not always exist. For a given intensity of current the quantity transformed reaches a maximum for a definite distance of electrical discharge; this maximum varies with the pressure. In order to obtain a satisfactory reaction the current must act simultaneously on both liquid and gas. Prolonged action of the current causes polymerization and the reactions become quite complicated. The apparatus can be used for deodorizing fish oil, as the unsaturated compounds of this oil take up hydrogen under these conditions. Because of the gradual polymerization produced the method is sug-

¹ *Bull. Soc. Chim. Belg.*, 26, 55.

gested as applicable for thickening mineral oils or mixtures of mineral oils with animal or vegetable oils. Molecular weights as high as 2500, as determined by the ebullioscopic method, were obtained. The viscosity of these polymerized oils varies less with the temperature than does that of the pure mineral oils; the coefficient of friction of the former is also stated to be less.

5101. The shortage of lubricating oils in Germany during the War led to an examination of the De Hemptinne process. The result was the production of what are known as Voltols. Wolf ² says that the Olwerken Stern Sonneborn, now known as Rhenania Ossag Mineralölwerke A.-G. Hamburg, makes these artificial polymerizates on the large scale by the action of the silent electrical discharge upon mineral and fatty oils. Nernst, investigating the principles upon which the process rests, was convinced that hydrogen atoms were split off from the oil molecules by collision with gas ions and the new molecules thus formed were combined into larger molecular complexes. Eichwald and Vogel determined molecular weight and iodine number of olein voltolized in a nitrogen atmosphere. The mean molecular weight increased greatly, the iodine number dropped. Eichwald obtained molecular weights up to 6000 from the benzol solution of the oil.

5102. The technical process is conducted in large closed cylindrical kettles at a vacuum of 60–70 mm. and at about 80° C. (176° F.). The oil to be treated flows over the aluminum electrodes and is thus exposed to the electrical discharge. High-frequency alternating current at about 5000 volts is used and an inert gas, usually hydrogen or nitrogen, prevents oxidation. The viscosity can be raised at will. Voltols with viscosity up to 32° E. at 100° C. are still fluid at ordinary temperatures and have a good cold-point. The high viscosities are obtained with no loss of material and the acid number, asphalt content, cold-point, and color of the polymerizates remain unchanged; the flash-point rises only a little in proportion to the great increase in viscosity. Mineral and fatty oils or mixtures of the two, and low-temperature tar can be treated.

5103. Tests of the voltols on power-generating and power-transmitting machines with electric drive, continuous operation, showed power savings of 16.5 per cent; on a 10,000-h.p. triple-stage steam engine, oiling the working parts, fresh oil, drop oiler, an oil saving of 62 per cent, cost saving 25 per cent; on a 6700-h.p. Voith two-stage Pelton turbine connected with generator, heat from friction reduced 25 per cent; on a 2700-h.p. Leobersdorfer two-stage turbine, frictional heat reduced 53.1 per cent.

5104. An advance in lubrication of explosion motors is possible by voltolization, since the same oil will serve in any type of motor and in winter as well as summer. The oiling of explosion cylinders makes greater demands upon a lubricant than does bearing lubrication on account of the high temperatures obtaining in the cylinders; and a motor lubricating oil must burn as nearly without residue as possible. Even during the War voltol oil proved itself an excellent substitute for castor oil in aeroplane lubrication.

5105. Cylinder oils emulsified with water are not only protected against vaporizing and decomposition but are atomized in the cylinder. At first lime water

² *Petroleum*, Jan. 16, 1929, 95.

was used as the emulsifying agent, so that the emulsion consisted of three components. But voltol cylinder oils form a stable emulsion with water alone, which is a means of rational cylinder lubrication.³

5106. Fatty Acids and Glycerides: Action of the Brush Discharge.⁴ If oleic acid is subjected to the action of the brush discharge the iodine value steadily falls, the mean molecular weight steadily rises, and stearic acid is produced. The increase in molecular weight per unit fall in iodine value rises from 6.3 at the beginning of the treatment to 43.5 after treatment for twenty-two hours. About 11 per cent of the oleic acid is converted into stearic acid, and this conversion occurs in an atmosphere of air or nitrogen as well as in an atmosphere of hydrogen, though working under the latter conditions gives the slightly higher maximum yield of 15 per cent of stearic acid. It is considered that the bombardment of the molecules causes hydrogen atoms to become detached in a highly active state, and that they immediately saturate the double bonds of other molecules of oleic acid, leaving some highly unsaturated molecules which polymerize and cause the increase in molecular weight. Glycerides show similar effects under the brush discharge, the glyceryl part of the molecule being unaffected. The resulting polymerized oils have high viscosities and flat viscosity temperature curves and are of value as lubricants. Owing to the possibility of intra-molecular saturation of double bonds in the case of glycerides, the increase of molecular weight in this case becomes even more marked in the later stages of treatment than in the case of the free fatty acids.⁵

5106A. Decoic, lauric, palmitic, and stearic acids are polymerized by the action of the silent electric discharge for 30 to 100 hours in an atmosphere of hydrogen into viscous liquid acids, iodine values of 5 to 8, lower saponification and neutralization values and higher density.^{6a}

5106B. Oleic, linoleic, and linolenic acids when exposed to a silent discharge of 10,000 volts in gaseous media are attacked the more severely the smaller is the molecular weight of the gaseous medium. Hydrogenation and polymerization occur rapidly in hydrogen, slowly in nitrogen, and not at all in sulphur dioxide and carbon monoxide. As compared with the reaction in hydrogen, the rate of polymerization in nitrogen is much greater than that of hydrogenation in this gas.^{6b}

5106C. Experiments on oleic acid show that hydrogenation in the silent discharge increases in intensity with temperature between 15° and 95°; it increases with voltage between 5000 and 20,000 volts; it decreases with increase of distance between the electrodes between 3 mm. and 20 mm. under 10,000 and 20,000 volts; it decreases with increase in gas pressure between 0.006 and 10.0 mm. and increases with pressure between 100 mm. and 600 mm.^{6c}

5107. Action of the Silent Electric Discharge on Fatty Oils. (Voltol Process.)⁴ The chemical and physical properties of oils produced by the electrical treatment of fish oils by the "Voltol" process were investigated. The process comprises the treatment of fish oils in cylindrical iron vessels of 30 cu. m. capacity, capable of rotation about a horizontal axis. The electrodes, which are attached to the axis and pick up the oil from the bottom of the vessel, consist of a number of alternating aluminum and glazed cardboard plates, the aluminum plates being connected with a high-tension circuit (4300-4600 volts, 500 periods), so

³ *Univ. Oil Prod. Co. Bulletin*.

⁴ Eichwald, *Z. angew. Chem.*, 1922, **35**, 505; *Chem. Abst.*, 1923, **17**, 60.

⁵ *J.S.C.I.*, 1922, **41**, 824A.

^{6a} Iwamoto, *J. Soc. Chem. Ind. Japan*, 1930, **33**, 25-7B; *Brit. Chem. Abst.*, 1930, 451B.

^{6b} *Idem.*, *ibid.*, 1929, **32**, 259-60B; *Brit. Chem. Abst.*, 1930, 291B.

^{6c} *Idem.*, *ibid.*, 1929, **32**, 359-61B; *Chem. Abst.*, 1930, 2320.

⁷ Hock, *Z. Elektrochem.*, 1923, **29**, 111; *J.S.C.I.*, 1923, **42**, 508A.

that they alternately become charged positively and negatively, the glazed cardboard acting as dielectric. The oil is heated to 60°–80° C. and continually flows down the plates in a thin stream. The remainder of the vessel is filled with hydrogen at a pressure of 0.1 atmosphere. After several hours' treatment a maximum viscosity of the oil ("half voltol") is attained. If an equal quantity of mineral oil is then added and the treatment continued an exceedingly viscous "full voltol" is obtained. The characters of the original fish oil, "half voltol," and "full voltol" were as follows: mol. wt. 870, 1100, 650; specific gravity at 15° C., 0.9224, 0.9365, 0.9371; $n_D^{15} = 1.4661, 1.4708, 1.4892$; iodine value, 129–8, 88.6, 42.5; saponification value, 195, 196, 107; viscosity at 21.8° C., 68 secs., 1100 secs., —; viscosity at 100° C. 8.8 secs., 96 secs., —. The ions and electrons forming the electric discharge appear to disrupt the molecules of the unsaturated glycerides at the double bond and to cause the formation of polymerized molecules which form a colloidal solution to a greater or less degree. The great increase in viscosity of the oils after treatment is probably caused by the colloidal nature of the solution of polymerized molecules. Oil subjected to the voltol process in a laboratory apparatus was polymerized to a higher degree than the product of the commercial process, but ultra-filtration showed that the latter product had assumed to a greater extent the colloidal state. The commercial product also showed a permanent decrease in viscosity after having been subjected to a temperature of 200° C. for some hours. This is ascribed to a reversion from the colloidal state. Experiments with gases other than hydrogen showed that better results are obtained with hydrogen than with either argon or nitrogen, but that hydrogen is by no means essential to the process.

5107A. A description of the Voltol process and a bibliography are given by Zakharenko.^{6a}

5108. Becker⁷ has observed that when mineral or fatty oils are subjected to the silent discharge not only does an increase of viscosity occur but also, from saturated hydrocarbons, an evolution of hydrogen. Becker proposes this method for the production of hydrogen of the highest purity. He points out that from inorganic compounds also hydrogen is evolved under similar treatment.⁸

5108A. On passing a high-tension discharge^{8a} through a saturated paraffin oil in a Siemens ozonizing tube, hydrogen is evolved and higher paraffins are formed. Under the same conditions unsaturated hydrocarbons yield mixtures of saturated hydrocarbons of high molecular weight, the hydrogen evolved in the first reaction being absorbed again at the double linking.

5109. Not all the processes about to be described are essentially hydrogenations. They are, however, potentially convertible into hydrogenations. Because of this and because of the interest which has been recently shown in processes of this character, they are dealt with here.

5110. The application of a high-tension electric discharge for the purpose of increasing the proportion of fixed gases, in gases or vapors obtained by the cracking of oils has been proposed by Davidson and Ford.⁹

5111. They state that the constitution of the hydrocarbon components in a gas of this character may be materially changed by the action of the electric discharge, the general effect being the formation of bodies of less molecular weight which are not condensable, thus increasing the proportion of fixed hydrocarbon constituents of the gas as compared with the other components, such as hydrogen or carbon monoxide. In tests which were made the

^{6a} *Neftyanoe Khozyaistvo*, 1929, 16, 544–7; *Chem. Abst.*, 1929, 4809.

⁷ *Wiss. Veröff. Siemens-Konz.*, 1926, 5, 160. A similar effect has been reported by Schoepfle and Connell as a cause of cable deterioration (*Ind. Eng. Chem.*, 1929, 21, 529).

⁸ Further references on voltols: Brückner, *Chem. Ztg.*, 1928, 52, 637; Anon., *Ind. Olii Grassi*, 1926, May 31; *Chim. et ind.*, Apr., 1928, 661; *J.S.C.I.*, 1928, 974; Hock, *Kautschuk*, Mar., 1928, 65; this last article refers to a fatlike product obtained by subjecting rape oil to the Voltol process.

^{8a} Becker, *Wiss. Veröff. Siemens-Konz.*, 1929, 8, (2), 199–217; *Brit. Chem. Abst.*, 1930, 402B.

⁹ U. S. Pat. 1,229,042, June 5, 1917.

amount of methane in the gas was increased from 25 per cent to about 40 per cent, while the amounts of $C_{12}H_{22}$ were increased from between 7 and 10 per cent up to 20 and 23 per cent. In carrying out this process, apparatus which is similar to that used for the electrical precipitation of suspended matter from gases may be employed.

5112. Cherry¹⁰ describes a method for the production of hydrocarbon compounds by a synthetic process involving the use of a high-frequency electric current. He states that a rearrangement of the molecular structure of a hydrocarbon can be brought about to change the boiling-point and gravity, by subjecting the hydrocarbon to the silent discharge of a bipolar oscillatory high-frequency electric current and the boiling-point and gravity of the compound produced can be varied by varying the frequency of the current applied; and furthermore, a relatively low-gravity hydrocarbon can be so changed as to produce a compound of higher gravity and of lower boiling-point by subjecting such low-gravity compound to the electric discharge when the low-gravity hydrocarbon is in a vaporized state and mechanically mixed with a small proportion of a high-gravity low boiling-point hydrocarbon while a high-gravity low boiling-point hydrocarbon (such as casing head gasoline) can be so changed as to produce a product of lower gravity and higher boiling-point, by the action of the electric discharge while the high-gravity hydrocarbon is in a vaporized state and mechanically mixed with a small proportion of a relatively low-gravity high boiling-point hydrocarbon.

5113. In practicing Cherry's process, the vaporized or gaseous hydrocarbon material is passed through a bipolar oscillatory high-frequency silent electric discharge, and a rearrangement of the molecular structure is stated to be thereby brought about to either increase or decrease the proportion of hydrogen in the resulting compound without the waste incident to destructive distillation. The vaporized or gaseous hydrocarbon may be passed through a peculiar electric field or an electric treating chamber provided with separated electrodes between which the hydrocarbon body flows so that this body will be subjected for a more or less extended period of time to the silent electrical discharge oscillating back and forth between the electrodes.

5114. As an example of the application of the method to hydrocarbon compounds of the paraffin series, one volume of pentadecane ($C_{15}H_{32}$) is introduced into a still, to every two volumes of methane (CH_4) and the mixture of the resulting vapor and gas rising from the liquid in the still is passed through an electric field under proper heat and pressure conditions, a resulting liquid product being drawn from a condenser consisting of octane while the excess of methane is separately collected. In this instance, approximately the following reaction is claimed to take place.



5115. Northrup¹¹ passes the vapors of heavy hydrocarbons with gas containing hydrogen (e.g., natural gas) through an electrified zone (A. C. field 2000-8000 volts) where ionization takes place. The vapors are next led through catalyst tubes (5 per cent iron, 5 per cent aluminum) at 385°-538° C. Thence they go to a dephlegmator and condenser. The condensate at 93°-204° C. is returned, while the residual vapors are passed to a cool condenser and gasoline is obtained.

5116. Feige¹² treats solid, liquid, or gaseous fuels with high-voltage electric current preferably in an atmosphere of hydrogen, with tin as catalyst. In this way, for example, a brown tar containing only 4 per cent of constituents boiling under 200° C. can be made to yield more than 40 per cent boiling below 200° C.

5117. Ruben¹³ passes a liquid having a high dielectric constant upwards through a metal cylinder in which is suspended a porous pot through which a gas with a lower dielectric constant than that of the liquid is introduced. The pot is provided with a conductive inner surface, which is connected to one pole of a source of high-frequency, high-potential alternating current, and the metal wall of the outer cylinder is connected to the other pole. Reaction between the gas and the liquid is in this way induced without the use of a catalyst; for example, oils can be hydrogenated without the use of nickel.¹⁴

5118. At least two quite disparate processes seem to be described in the following: The Continental Caoutchouc and Gutta Percha Co. heat a mineral oil fraction of high boiling-point with a catalyst such as aluminum chloride, with or without mercuric, ferric, vanadium,

¹⁰ U. S. Pat. 1,229,886, June 12, 1917.

¹¹ Brit. Pat. 275,120, Mar. 21, 1927; U. S. Pat. 1,642,624, Sept. 13, 1927.

¹² Brit. Pat. 271,473, May 19, 1926; *Chem. Abst.*, 1928, **23**, 1672.

¹³ U. S. Pat. 1,554,296, Sept. 22, 1925; Brit. Pat. 251,134, June 16, 1925.

¹⁴ *J.S.C.I.*, 1925, 999B; *Brit. Chem. Abst.*, 1926, 553B.

or other chloride, or with aluminum in a stream of dry hydrochloric acid gas, or the oil is atomized and exposed to ultra-violet rays or the silent electric discharge in presence of a catalyst. The process is continuous. Gaseous products are obtained by heating to a higher temperature, and longer, in closed vessels.¹⁵

5118A. Lubricating and insulating oils are obtained from coal tars, mineral oils and other carbonaceous materials by extracting or destructively hydrogenating the solid materials or cracking or destructively hydrogenating the liquids, and exposing the liquid products or their fractions, in liquid phase, to the action of high-tension and preferably high-frequency electric currents.^{16a}

5119. Two closely similar processes are due to Epner.¹⁶ They are electrical processes for the production of lubricants and of fuel from hydrocarbon gases. According to (1) oils, suitable for use as lubricants, are obtained by subjecting methane, gases containing methane, gases obtained in cracking hydrocarbons, or ethane or ethylene from coke-oven gases to the action of an alternating electric field preferably of high frequency and high voltage. The products may be hydrogenated.

5119A. In the second process (2), liquid hydrocarbons, suitable as power fuels, are obtained by subjecting gases containing hydrocarbons to the action of dark or silent electric discharges, preferably of high tension and periodicity. The reaction is carried out at increased temperature so that the products are removed in vapor form and may be separated by cooling, by absorption in active carbon or in wash oils. The unsaturated products may be hydrogenated, preferably by passing the vaporous products from the reaction which already contain hydrogen over a heated catalyst.¹⁷

5119B. Epner proposes an apparatus for effecting this exposure of oils to dark electric discharges in which the electrodes are liquids boiling above 100° C. These may be circulated. The vessels containing them should be made of a material, such as quartz, whose dielectric properties are unaffected by temperature changes.¹⁸

5119C. Production of Liquid Polymerization Products from Gases Containing Hydrocarbons.^{18a} Methane, or gases containing methane, are subjected to the action of an alternating, high-tension electric field producing a silent electric discharge. The reaction is carried out in the presence of catalysts which promote condensation or hydrogenation, and at temperatures, e.g., 150–500°, at which the products are in the form of vapor or a mobile liquid.

5120. Walker¹⁹ claims the combined application of a high-tension electrical discharge and of catalytic action in the hydrogenation of oils. In Fig. 118, 1 is the reaction chamber; 2 is a hollow metal plate serving as an electrode; 3 is an inlet and 4 an outlet for superheated steam; the face of the plate is covered with catalyst (e.g., nickel or nickel oxide); 5, 5' are plate electrodes; 6 is a source of high-tension current one terminal of which is connected with 5 and 5', the other with 2. By means of an injector 10, hydrogen and oil are caused to impinge

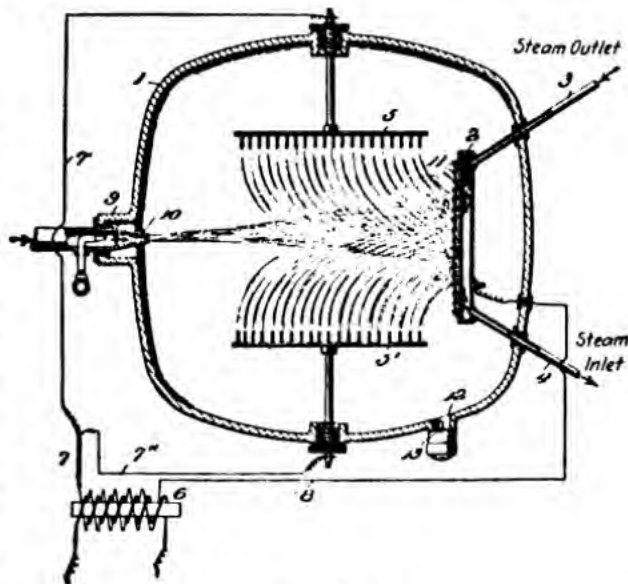


FIG. 118.

¹⁵ French Pat. 469,948, Mar. 21, 1914; *Chem. Abst.*, 1915, 9, 19.

^{16a} I. G. Farbenind. A.-G., Brit. Pat. 305,553, Oct. 5, 1927; *Chem. Abst.*, 1929, 4814.

¹⁶ Brit. Pats. (1) 294,099 and (2) 294,100, convention date, July 16, 1928.

¹⁷ *Ill. Off. Jour.*, Sept. 12, 1928.

¹⁸ Brit. Pat. 296,019, Aug. 23, 1927.

^{18a} Epner, Brit. Pat., 317,344, May 9, 1928; *Brit. Chem. Abst.*, 1929, 844B.

¹⁹ U. S. Pat. 1,123,962, Jan. 5, 1915; *Chem. Abst.*, 1915, 729.

against the catalytic surface in the electrical field. Walker claims that hydrogenation is thus obtained without the deleterious effects of long exposure of the oil to high temperature.

5121. Utescher treats oils with hydrogen in presence of a finely divided catalytic agent, and at the same time the material is subjected to the action of a silent electric discharge. In a description of the process, it is stated that the "silent discharge" is prevented from coming into actual contact with the fatty substance, only chemically active rays (e.g., from a mercury vapor lamp) being utilized. It is also stated that the process may be effected by allowing the rays to impinge on the surface of a catalytic substance, which may be used in the form of plates. The joint application of a catalytic and an electric discharge is claimed to give a greater effect than either agent singly.²⁰

5122. In the Grüner processes²¹ oils or fats are subjected to the action of a silent electric discharge of very high tension and frequency in an acid atmosphere. The voltage used is 50,000-100,000.

5123. Wielgolaski²² brings hydrogen into contact with fats or fatty acids while exposing the material to Roentgen rays, and in the later patent while subjecting it to electrical action as it passes through porous electrodes.

5124. Experiments were performed by Custis²³ to ascertain if there would be an acceleration of the hydrogenation of oleic acid under the influence of the rays from an iron arc. The hydrogen was led into a quartz flask, which contained the oleic acid. A long air condenser was passed through the stopper with which the flask was supplied. An iron arc was placed 1.5 cm. from the flask, and exposure was allowed to proceed for six hours. From the iodine numbers of the acid before and after treatment the conclusion was reached that there is no acceleration in the hydrogenation of oleic acid when hydrogen acts on the acid in the presence

of rays from an iron arc under ordinary conditions of temperature and pressure. Blank experiments showed an amount of saturation equivalent to that found in the exposed fatty acid.

Some observations on the effect of ultra-violet light on catalytic action have been made by Farmer and Parker which indicate that on colloidal platinum, at least, the ultraviolet light exerts a retarding influence on the rate of catalytic change. Colloidal platinum was prepared by the Bredig method, i.e., by producing an arc between platinum electrodes under distilled water. Hydrogen dioxide was used as a measure of catalytic activity. The colloidal platinum was exposed to the ultraviolet light and samples were drawn from time to time in order to get exposures of varying lengths, the samples being introduced into hydrogen perox-

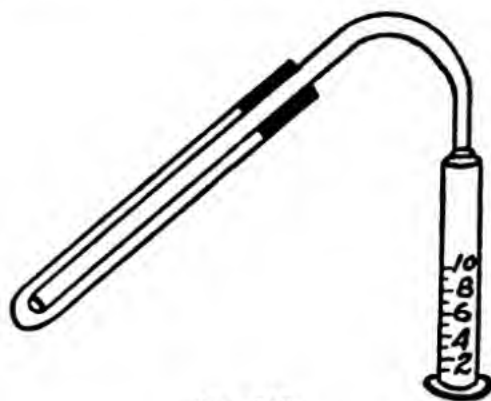


FIG. 119.

ide placed in an apparatus shown in Fig. 119. The inclined tube of this apparatus was completely filled with dilute hydrogen peroxide solution and a bent delivery tube arranged to collect any liquid displaced. As colloidal platinum breaks down hydrogen dioxide yielding oxygen, the evolution of the gas and consequent displacement of liquid enabled the rate of decomposition to be measured.

The experiments showed that the catalytic activity of the colloidal platinum was almost completely destroyed after an exposure of six hours, the activity then observed being no greater than that of the spontaneous decomposition of hydrogen peroxide itself. It was noted that the light caused the platinum to be precipitated out of solution as a black flocculent material. After such a precipitation it was in the form of large mossy clusters.

While no observations were made with respect to the hydrogenation of oils under these conditions, in view of the action of ultraviolet light on solutions of colloidal platinum, it

²⁰ Brit. Pat. 20,061, Sept. 3, 1912. The text of the Utescher Ger. Pat. 266,662, 1912, appears in *Chem. Rev. u. d. Fett u. Harz Ind.*, **1913**, 308.

²¹ French Pat. 453,664, Jan. 27, 1913; Holl. Pat. 1,142, Feb. 4, 1916; *Chem. Abst.*, **1916**, 1725.

²² Norw. Pats. 24,528 and 25,009; *Seifen. Ztg.*, **1914**, 1195.

²³ *J. Frank. Inst.*, 1917, 880.

would appear that exposure thereto may be expected to modify the rate of reaction in the hardening of oils.^{23a}

5125. Aromatic Hydrocarbons from Coal. Though applied to solid raw materials the process²⁴ described below fits in more appropriately here than elsewhere. Aromatic hydrocarbons are produced from carbonaceous materials (e.g., powdered bituminous coal with or without admixture with limestone) by heating in a retort and subjection to a high-frequency oscillating electromagnetic field in the presence of hydrogen. The carbon particles suspended in the gas become ionized and react, yielding enriched hydrocarbon gas.²⁵

5126. Preactivation of Hydrogen. Fuchs²⁶ claims that his investigations have shown the present methods of reduction for the most part to be improperly founded, causing long time of treatment coupled with loss of hydrogen and heat; use of a great excess of hydrogen or catalyzer; injurious action of the long heating on the color, taste and odor of the reduced fat; and the application of high pressure in apparatus which involves costly autoclaves, dangerous to handle. Fuchs declares that the conduct of reduction of fatty bodies is essentially improved if the following theoretical conditions are observed:

(1) Thermal considerations: A quickening of the reaction is obtained when the oil to be treated is maintained at only a moderate temperature (0° to 150° C.), while the hydrogen employed is heated to 200° to 250° C. The avoidance of strong heating of the oil which is being treated is favorable to the quality of the final product, while preheating the hydrogen appears to increase its activity. Comparative tests show that in this way the speed of the reaction can be increased by about 10 per cent. For preheating the current of gas, copper or nickel coils in an oil bath are used. The oil bath may be maintained at the requisite temperature through circulation of oil heated at a distant point.

(2) Chemical considerations: Since it is impossible to have free hydrogen in its most active form, that is, in a nascent state, act upon the oil to be treated, because the quality of the oil is injured, Fuchs observes that means must be provided to apply the hydrogen in the atomic form. This can be carried out through the application of chemically active rays. Dissociation of the hydrogen molecule appears also to occur when molecular hydrogen is passed over catalytic material such as palladium-black or freshly prepared nickel powder and then is allowed to diffuse under high pressure through heated plates of metal. The activity of the dissociated hydrogen, it is claimed, is from 15 to 20 per cent higher than the normal gas. The catalytic material may be placed in a tube of suitable length or on the plates of a column apparatus. By way of illustration Fuchs states that cottonseed oil carrying 0.9 per cent of a catalyzer, prepared from nickel carbonate, is raised to a temperature of 120° and is subjected to hydrogen under a pressure of 18 atmospheres, the gas having been chemically activated by passage through an iron tube 3 meters in length and 60 mm. in diameter, lined with platinized asbestos and heated to 250° C. In this way by two hours' treatment a fatty body having a melting-point of 44° C. was prepared. In three hours a fat melting at 65.4° C. was obtained. Fuchs notes that ordinarily from five to eight hours would be required to secure such products. The claims of Fuchs' patent call for the reduction of unsaturated fatty acids and their glycerides by means of hydrogen according to the contact process, wherein strongly heated hydrogen is caused to react on only moderately heated oil; also the treatment of oil with atomic hydrogen whose activity has been increased by treatment with chemically active rays.

5127. Vogel²⁷ claims a process for treating carbon compounds (e.g., unsaturated fatty oils) with ionized gases (e.g., hydrogen) whereby hydrogenation takes place. This is effected by spraying or frothing the oil with the hydrogen in a vessel containing a means of producing an alternating electric field of high frequency and voltage.²⁸

5128. By passing light hydrocarbon vapors through an arc struck between two tubular electrodes in an atmosphere of hydrogen and carbon monoxide,

^{23a} *J. Am. Chem. Soc.*, **1913**, 1524. Experiments made by Ellis point to a reduction of the iodine value of cottonseed oil exposed to ultraviolet radiation in presence of hydrogen. Cf. U. S. pats. 1,180,025, Apr. 18, 1916 and 1,179,414, Apr. 18, 1916 to Ellis.

²⁴ Brit. Pat. 267,359, May 28, 1926, to Henry.

²⁵ *Brit. Chem. Abst.*, **1927**, 357B.

²⁶ *Seifen. Ztg.*, **1913**, 982; *ibid.*, 1298. Reduction of unsaturated fatty acids and their glycerides, Belgium Pat. 256,574, 1913.

²⁷ U. S. Pat. 1,621,143, Mar. 15, 1927.

²⁸ Other applications of the principle are given.

heavier hydrocarbons are produced, e.g., $C_2H_4 + CO + 2H_2 = C_3H_8 + H_2O$ and $C_2H_4 + CO + 2H_2 = C_4H_{10} + H_2O$. The reaction chamber may be filled with a catalyst (finely divided metals) and heated.²⁹

5129. An article by Evers deals with the effect of the electric arc on mineral oils.³⁰

5130. Siemens and Halske³¹ use the hydrogen generated by passing an alternating electric discharge through liquid hydrocarbons to produce frothing.

5131. Jakosky. Effects of corona discharge on petroleum. *U. S. Bureau of Mines, Tech. paper*, 375.

5132. A proposed cracking and hydrogenating process³² yielding motor fuel and lubricating greases from an oil such as kerosene, comprises heating the oil under a hydrogen pressure of 300 to 500 lbs. per sq. in. and in presence of an electrolyte such as aqueous sodium chloride and pieces of copper and zinc. The electrochemical action of the zinc-copper couple is supposed to facilitate the conversion.

²⁹ Brit. Pat. 223,543, Sept. 22, 1924, to Le Pétrole Synthétique, assignees of Andry-Bourgeois.

³⁰ *Wiss. veröffentl. Siemens-Konzern*, 1925, 4, 324; *Chem. Abst.*, 1926, 3075.

³¹ French Pat. 615,581, May 4, 1926, to Siemens und Halske A.-G.

³² Maxim, Brit. Pat., 118,122.

CHAPTER LII

OTHER HYDROGENATIONS AT HIGH PRESSURES

5200. Catalytic Hydrogenation at High Pressures.¹ The majority of hydrogenation processes are conducted at atmospheric pressure or at a plus pressure of a few atmospheres. Nevertheless hydrogenation at very high pressures, though industrially a development dating back but a few years, is not a novelty in the laboratory, as the following examples will show:

5201. Ipatiev² finds that in presence of nickel oxide, indene unites with hydrogen at 250° to 260° C. and 110 atmospheres, yielding the hydrocarbon octahydroindene. The nature of the metal of which Ipatiev's high-pressure apparatus³ is constructed is found to exert an influence on the hydrogenation, in presence of cuprous oxide, of compounds containing ethylene linkages. Thus, in an iron tube, amylene (trimethylethylene) is readily converted into isopentane, while in a copper tube the reaction is incomplete, an equilibrated mixture of amylene, hydrogen and isopentane remaining:



In an iron tube and in absence of cupric oxide, no hydrogenation occurs. Similar results are obtained with hydroaromatic compounds. Further, hydrogenation in an apparatus of phosphor-bronze in presence of reduced copper results in the establishment of an equilibrium, while, if iron turnings are also present, hydrogenation proceeds to an end. The catalytic activity of reduced copper in copper tubes may be regarded as due to poisoning of the catalyst; or the use of cupric oxide in iron tubes may result in a conjugated catalytic action.

5202. Carbon and hydrogen combine with difficulty, especially to form methane. At the ordinary pressure in the presence of nickel oxide, reduced nickel or a mixture of nickel and alumina, and up to 624° C., there is no formation of methane. Under great pressures the synthesis occurs only above 500° C. in the presence of the above catalysts. In the presence of water and nickel, methane is decomposed at 500° C. into hydrogen and carbon dioxide.

5203. The reverse reaction, i.e., the reduction of carbon dioxide to methane in the presence of nickel and an excess of hydrogen at ordinary pressure, occurs at 450° C.⁴ Sabatier showed that methane is readily prepared in approximately theoretical yield at ordinary pressures, and at temperatures ranging from 230–400° C.⁵

5204. Acetylene is converted into ethylene by treatment with hydrogen under pressure in the presence of catalysts. The Elektro Chemische Werke G. m. b. H.⁶ state that to effect the combination of the unaltered ethylene and hydrogen in the gaseous mixture resulting from the passage of these gases over a catalyst, the product is again passed over the catalyst under pressure. The reaction is stated to be quantitative and instantaneous. Nickel or metal of the platinum group may be used as a catalyst.⁷

5205. Hydrogenation in the liquid phase under very high pressure is associated with the name of Ipatiev.

¹ A valuable article on high pressures in chemical industry, from the pen of Maxted, appears in *Chem. and Ind.*, 1926, 45, N. S. 366. An article by Ernst (of the Fixed Nitrogen Research Laboratory), in *Ind. Eng. Chem.*, 1926, 18, 664, describes and illustrates the mechanical equipment for high pressure and discusses the metallurgical problems involved.

² *J. Russ. Phys. Chem. Soc.*, 1913, 45, 994.

³ *J.S.C.I.*, 1911, 239.

⁴ *Chem. Trade Jour.*, 1913, 414.

⁵ Sabatier. *Catalysis*, 396. Ipatiev, *Chem. Ztg. Rep.*, 1914, 15.

⁶ *Zeit. f. angew. Chem.*, 1913, Ref. 644.

⁷ Ger. Pat. 265,171, Oct. 16, 1912.

5206. The method of Ipatiev consists of heating the substance to be hydrogenated and the catalyst in hydrogen in a vessel capable of sustaining an internal pressure of 600 atmospheres.

5207. The catalyst is nickel or "nickel oxide." Ipatiev believed the latter to be, in the conditions of the method, the better catalyst of the two. Many chemists now hold, with Sabatier,⁸ that the activity of the catalyst is due to its content of metallic nickel. It is probable that, with the manipulative methods employed by Ipatiev, the formation of metal by reduction of the oxide *in situ* furnished a more active catalyst than was obtained by an external reduction and possible incandescence and sintering during the transfer. It is possible, though less probable, that nickel oxide, in the particular reactions in which the comparison was made, exerted a promoter action. It must also be remembered that the conditions of complete reduction to metal are unfavorable to the highest catalytic activity. Other catalysts used by Ipatiev were palladium, iron, copper and its oxide and, occasionally, zinc dust.

5208. Ipatiev's typical apparatus consisted of a mild steel tube lined with copper, capable of sustaining a pressure of 600 atmospheres at 600° C., provided with a manometer, and a safety valve. Heating was by electric resistance wires.

5209. The charged apparatus was filled with hydrogen at a given pressure and heated to the desired temperature. If no hydrogen were absorbed and no gas evolved the pressure would rise proportionately to the increase of temperature. But if hydrogen were absorbed there would be a relative fall of pressure (unless there occurred a compensatory evolution of some other gas).

5210. For the ordinary purposes of organic chemistry and for experimental work on the hydrogenation of oils the expensive, limited and rather dangerous method of Ipatiev has been replaced by processes using moderate pressures. Nevertheless it must be regarded as one of the immediate ancestors (an other being the Haber ammonia process) of processes which are already of cardinal importance and whose recent development has been sensational. These are the processes for the synthesis of methanol and its higher homologs (by hydrogenation of water-gas), and for the hydrogenation of coal and other substances for the production of fuel oil (Bergius processes, or berginization). The processes of the first group are worked, however, in the gas phase.

5211. The principal object attained by the use of high pressure in autoclave processes is usually the maintenance of the liquid phase at high temperatures. For example, water at 300° C. maintained in the liquid condition by high pressure is an active chemical, and if in this condition it is allowed to act on iron, in the presence of thallium chloride, hydrogen is produced.

5212. Pressure and Chemical Equilibrium. The effect of pressure on chemical equilibrium was clearly enunciated by Robin⁹ as follows: "For constant temperatures there is one definite pressure for which a system will be in equilibrium. On raising the pressure the reaction will proceed in that direction which is produced with a decrease in volume; while, if the pressure is reduced, the reaction will proceed in that direction which has a greater volume." Le Chatelier¹⁰ considered the problem of the shift of equilibrium with pressure and tempera-

⁸ *Catalysis in Organic Chemistry* (tr. Reid), 584.

⁹ *Bull. Soc. Philomath.*, 1879, [7], 4, 24.

¹⁰ *Compt. rend.*, 1884, 99, 786.

ture from the thermodynamic standpoint, and introduced the principle of mobile equilibrium. This principle states, in effect, that if a system in equilibrium be subjected to a constraint, a change will take place in the system which is in opposition to the constraint.

5213. In the case of gaseous reactions, pressure is employed to change the equilibrium in favor of the desired product. The attainment of this equilibrium, or the approach to it, is brought about by the use of catalysts.

5214. The reason for the use of high pressures in gaseous syntheses is clearly shown in the case of ammonia. Theoretically, it is quite possible to synthesize ammonia at ordinary pressure. Haber has calculated that if the temperature of the reaction could be reduced to 300°, satisfactory yields would be obtained under ordinary pressure. No catalyst is known, however, which will initiate the reaction at so low a temperature. The only choice in practice is to obtain a catalyst which is highly reactive at as low a temperature as possible, and then to raise the pressure to such an extent that adequate yields of ammonia result. While the Badische Anilin und Soda Fabrik have fixed on about 300 atmospheres as their working pressure, Claude has devised plant to work at a pressure of 900 atmospheres.

5215. The conditions for the production of methyl alcohol are governed by similar considerations. If a catalyst could be found which was highly reactive at as low a temperature as 200°, it is calculated, from certain data published by Audibert and Raineau,¹¹ that a satisfactory yield of methyl alcohol would result by conducting the syntheses at that temperature under atmospheric pressures. No catalyst has yet been found to work at so low a temperature, and high pressures have to be employed to give satisfactory yields.¹²

5216. The reasons for the use of high pressures in gas phase hydrogenations are: 1. To increase the reaction velocity by increasing the concentration of the reactants. 2. To modify the equilibrium in the desired direction. 3. To influence the reaction path. Perhaps the commonest case of this is the prevention of the decomposition of a desired product which, at the temperature used, would occur under lower pressure. 4. To facilitate heating and cooling, including heat exchange between gases in countercurrent. It is notoriously difficult to heat uncompressed gases with reasonable efficiency; very large heating surfaces are required. When gases are greatly compressed the problem is simplified. Nitrogen at 250 atmospheres has a density about one-third that of water and behaves in many respects like a mobile liquid.¹³ There is some evidence that pressure facilitates the treatment of bodies which contain catalyst poisons.¹⁴

¹¹ *Ann. office combustibles liquides*, 1927, 4th part.

¹² Morgan, Taylor and Hedley, *J.S.C.I.*, 1928, 47, 117T.

¹³ For an example of the method of estimating the temperature, pressure and equilibrium point of a reaction applied to a hydrogenation under high pressure see Kelley: A thermodynamic consideration of the synthetic methanol process. Morgan, *et al.*, *J.S.C.I.*, 1928, 47, 122T. Bone has stated that the chief advantages accruing from the use of pressure in connection with reversible chemical interactions are not merely to hasten the attainment of equilibrium but also, in changes involving diminution in the number of molecules, to cause the equilibrium to shift at a given temperature in that direction: for while an increase in temperature shifts the equilibrium in an endothermic direction, an increase in pressure usually has an opposite effect. Hence, by imposing pressure upon temperature, there results a speeding-up effect of the latter while diminishing its unfavorable influence upon the equilibrium proportion of the exothermic product. Further, by adding a catalyst, not only is the change accelerated, but in some cases also a new qualitative result may be induced. Therefore, when experimentally studying catalytic change in gaseous systems it becomes necessary not only to determine variations of equilibrium with both pressure and temperature, but also to ascertain the "directive influence" (if any) of various possible catalysts. As regards the latter, Bone observes that we are suffering from the present unsatisfactory and chaotic state of knowledge concerning the action of catalysts, an action which is much more complex than has been supposed. *Chem. Age* (London), 1930, 288. The comments by Bone (Discussion on Catalytic Reactions at High Pressures, *Proc. Royal Soc., A*, Vol. 127, 1930) also are of interest in this connection.

¹⁴ Maxted, *loc. cit.*

5217. The application of these relatively high pressures in industrial chemistry has, as already noted, a history of comparatively few years' duration. Already it has produced sensational results, and it is scarcely speculative to predict that this almost unexplored field will yield great returns to the chemists and engineers who ally themselves to exploit it. Incidentally, the term "high pressure" applied in this field is gradually undergoing a change in significance. In the earlier days of high-pressure experimentation, working in the neighborhood of 100 atmospheres was considered the height of daring. Ipatiev, it will be noted, used a pressure of 110 atmospheres. (See paragraph 5201.) His work was on a small laboratory scale. The commercial possibilities of such pressures were slow in making a beginning. The hazards appeared too great. Yet today numerous plants are engaged in industrial operations utilizing pressures of several hundred atmospheres; and this too with casualties surprisingly small. The trend is toward still higher pressures, all to such an extent that the term "high pressure" so freely used in relevant publications demands a revised definition. Michels would have us no longer in doubt. He states ¹⁴: "In general we refer to pressures up to 2500 atmospheres as low, pressures between 2500 and 10,000 atmospheres are regarded as medium, and pressures above 10,000 atmospheres are regarded as high." He also refers to preliminary work, consisting mainly of the examination of materials to stand "really high pressures" and then alludes to having reached pressures of 35,000 atmospheres.

APPARATUS FOR HIGH-PRESSURE WORK IN THE GAS PHASE

5218. The inventors and manufacturers working in the carbon oxides syntheses have been sparing in the publication of details of the construction of the plant. Most of the patent descriptions confine themselves to generalities, such as those relating to material for lining reaction vessels, and give little or nothing on the actual working designs. More is known of the construction of apparatus for nitrogen fixation, which presents somewhat similar problems. From publications in this field and from articles on work with apparatus of experimental and semi-commercial scale, information may be derived which is applicable to the design and construction of large-scale installations.

5219. Materials for High-pressure Reactions. The materials used in high-pressure hydrogenation must possess, in addition to high tensile strength, resistance to the corrosive action of the gases and vapors and to high temperature.

5220. Various patents, chiefly from the I. G. Farbenindustrie A.-G. or associated corporations, claim the use of certain materials for the methanol synthesis and for berginization. Thus, the Badische Company prescribes the use, in the methanol synthesis, of apparatus made of or lined with a metal or alloy which does not form carbonyls and which is resistant to the temperature of operation. Such materials are, for instance, copper, silver, aluminum and their alloys, special steels containing substantial amounts of chromium, manganese, tungsten, molybdenum, or vanadium, such as "steel V2A," or the metals chromium, manganese, tungsten, molybdenum, and vanadium themselves. Iron, nickel and cobalt must be excluded. To protect the reaction tube against the action of hot hydrogen, it may be formed of a steel wall with a lining of copper, or other suitable metals.^{15, 16}

¹⁴ *Proc. Royal Soc.*, 1930, A, Vol. 127.

¹⁵ *Chem. Abst.*, 1925, 19, 3490.

5221. British Pat. 249,155, Mar. 14, 1925, to I. G. Farbenindustrie A.-G., for berginization apparatus, is analogous to the Badische patent just summarized relating to apparatus for methanol synthesis.¹⁶ It is here specified that the apparatus must be refractory to carbon monoxide under the conditions of berginization. The materials mentioned are: copper, silver, aluminum or its alloys, chromium, manganese, vanadium or uranium steels or corresponding alloys of nickel or cobalt containing manganese, titanium, chromium, tungsten, vanadium or molybdenum. Tin, zinc, cadmium, lead and their alloys may be used in cooler parts.¹⁷ Note the mention of nickel and cobalt alloys.

5222. The British Pat. 277,273, Mar. 13, 1926, to the I. G. extends the application of 249,155 (just cited) to other parts of the apparatus than those mentioned in the latter. According to the earlier patent only the high-temperature zones were to be made of specially resistant metals (copper, silver, aluminum, chromium, manganese, vanadium or special steels). Experience showed, however, that even in the cooler zones carbon dioxide was decomposed and that the resulting monoxide attacked the walls with the formation of carbonyls. The same result may occur when the reactant gas introduced is only hydrogen, if the material treated is an oxygenated compound such as a phenol whose decomposition may lead to the formation of carbon monoxide. All parts of the apparatus, therefore, must be made of the specified materials or, in the case of low-temperature zone, of tin, zinc, cadmium or lead.¹⁸

5223. For the prevention of carbon deposit during berginization the apparatus may be lined with an alloy containing cobalt, molybdenum, tungsten, vanadium, manganese or nickel, together with boron, arsenic, antimony, silicon, bismuth, phosphorus or selenium. These alloys have also a catalytic function.¹⁹

5224. A manganese bronze wall catalyst is used in the hydrogenation of oils, tars, etc., at 450° C. and 200 atmospheres hydrogen pressure. A liquid product containing 25 per cent gasoline results.²⁰

5225. Maxted (*loc. cit.*) says little about any special construction material because he is dealing, in the article cited, with high-pressure work in general, and not with carbon oxide syntheses or with berginization in particular. He speaks of high-pressure vessels being of mild steel and says that they may be cast if an ample coefficient of safety is applied in the design, to allow for blowholes and other latent sources of local weakness. Ernst (*loc. cit.*) goes into considerable detail on the subject, and we shall draw largely on his article for what follows.

5226. The choice of materials lies among the carbon steels, alloy steels and non-ferrous alloys. While the tensile strength of carbon steel increases with increase of the carbon content,²¹ the greater cost in raw material and working of high carbon steels causes them to be but little use for high-pressure work. For these purposes the alloy steels are preferred. At present the most used alloying materials are nickel, chromium and vanadium. The presence of nickel greatly increases the tensile strength of steel and heat treatment adds immensely to this strength. Chromium has little effect in increasing the strength of steel but, if heat treated, a chromium steel is hard, tough, and resistant to corrosion. Vana-

¹⁶ Brit. Pat. 231,285. Cf. French Pat. 659,582, Aug. 28, 1928, to I. G.; *Chem. Abst.*, 1929, 5253.

¹⁷ *Chem. Abst.*, 1927, 21, 1002.

¹⁸ *Chem. Age* (London), 1927, 17, 351. See also Ger. Pat. 490,248, Feb. 25, 1923, to I. G. (Pier, Rumpf and Stein, inventors); *Chem. Abst.*, 1930, 2137.

¹⁹ *Chem. Age* (London), 1927, 17, 352; Brit. Pat. 275,662, by the I. G.

²⁰ Brit. Pat. 282,814, to the I. G. Zinc is permeable to hydrogen at 300°, and more so at 370°. It increases in crystal size after permeation. Copper is also permeable above 500° and the increase in crystal size probably causes the fissures which appear. Nickel is quite permeable to hydrogen at 470° and above, but there is no accompanying change in crystal size. Hendricks and Ralston, *J. Amer. Chem. Soc.*, 1929, 51, 3278.

²¹ Up to 0.83 per cent of carbon according to Sauveur, up to 1.4 per cent according to Dalby.

dium is usually employed together with chromium. For the ammonia converter, where high pressure, temperatures of 450°–500° C., and corrosive gases are found, an alloy steel containing 2.5 per cent chromium, 0.2 per cent vanadium and 0.37 per cent carbon, has been found effective. For still higher temperatures nichrome (nickel 80–85 per cent, chromium 20–15 per cent) has proved satisfactory. All steels seem to be at their maximum tensile strength between 250° C. and 300° C.

5227. Details of Construction.—Reaction Tube Head. Ernst shows three types of cylinder closure. In all the retaining bolts are in compression when under load. The bolt circle is as nearly as possible over the mean circumference of the gasket. These types are shown in Fig. 120. Type A, here shown on a tube $4\frac{1}{2}$ in. internal diameter is the best but is not practicable on small tubes such as are used in experimental work. B and C are equally good as regards strength and gas tightness, B being the less bulky and the cheaper: it should, however, not be used where the nut end would be, across flats, greater than 4 in. The largest

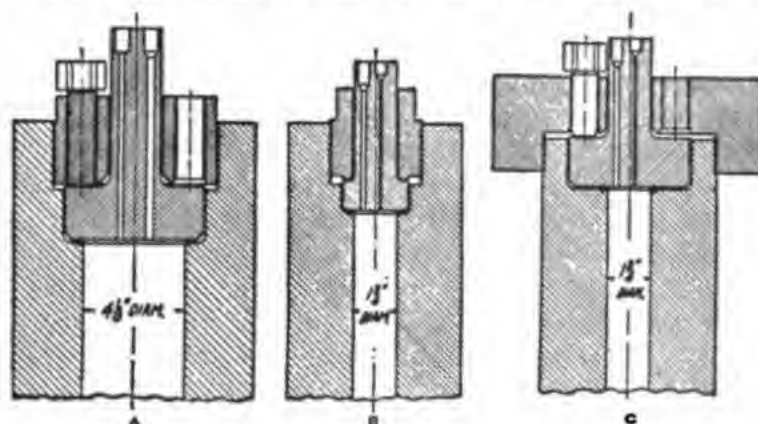


FIG. 120.

(From Ernst: *Ind. Eng. Chem.*, 1928, **18**, 667.)

bolts practicable should be used. The gasket material is copper, silver, or some other relatively soft metal which, actually flowing under pressure will fill the small V groove cut alike into the seat in the cylinder and into the head.²²

5228. With a similar, or identical construction problem Maxted (*loc. cit.*) deals in a different way. Of gas-tight fitting covers for cylinders he shows two types (Fig. 121). In the first the cover has a shallow cylindrical projection which fits into a recess on the machined end of the high-pressure vessel, the actual joint being made by a gasket. In the second type the gasket is in a rabbet cut round the inside of the cylinder end. The gasket may be of vulcanized fiber, lead, soft copper or aluminum. Fiber cannot be used for high temperatures, and lead has anti-catalytic properties. Formation of a gas-tight joint is facilitated by scoring both the projection and the recess with concentric circles. It is well to dress the surfaces in contact with graphite paste. An aperture of this kind should be made as small as is practicable, for the difficulty of securing a gas-tight union increases rapidly with increase in the opening.

5229. The greatest strength in a cover for a high-pressure vessel is given by an ellipsoid generated by an ellipse whose major axis is the diameter of the cover and whose minor axis is half that dimension.

²² A method for figuring such a gasket is given in *Ind. Eng. Chem.*, 1925, **17**, on pages 781–783. This is an admirable article on the construction and layout of a direct synthetic ammonia plant, by Ernst, Reed and Edwards; it is extremely detailed and should be consulted by everyone intending to construct a high-pressure equipment, for no matter what chemical operation.

5230. Tube Connections. Suitable tubing is obtainable commercially in almost all sizes up to a ratio of inside diameter : outside diameter :: 1 : 3. The Fixed Nitrogen Research Laboratory has used two sizes with special advantage, viz., $\frac{1}{8} \times \frac{3}{8}$, and $\frac{1}{8} \times \frac{1}{8}$. The

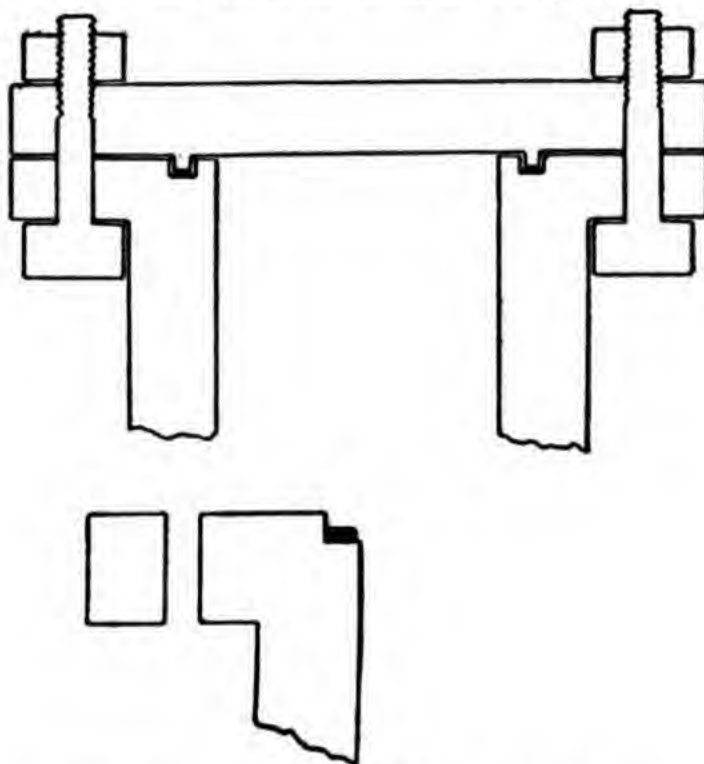


FIG. 121.

(From *Chem. & Ind. (J.S.C.I.)*, May 28, 1926, 366.)

smaller size is too small to stand threading for pressure work. It can be joined, however, without threading by the steel cone or the squeeze joint, both of which are shown in Fig. 122 (B). This kind of joint has proved satisfactory with pressures up to 1500 atmospheres,

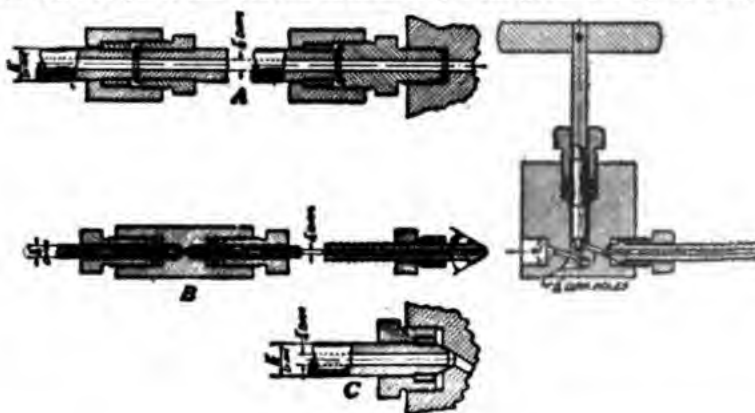


FIG. 122.

which is probably well below the upper limit. When the wall thickness permits of threading, joints such as are illustrated in Fig. 122 (A and C), are preferred by Ernst (*loc. cit.*). The pressures to be withstood are higher than those met with in the methanol and similar syntheses.

5231. For joining two tubes the method shown in Fig. 123 is advised by Maxted. The ends of the tubes are faced and screwed into a pair of flanges, one of these is recessed and the other carries a projection fitting into the recess. The end of each tube projects very slightly beyond the projection or the recess, respectively. A metal or graphited ring of vulcanized fiber is inserted and the joint tightened by the bolts. The actual joint is between the ends of the tubes and the gasket. Such a joint is suitable for pressures up to 250 atmospheres. Figure 124 shows how a similar joint may be used to connect a tube with a vessel of larger dimensions.

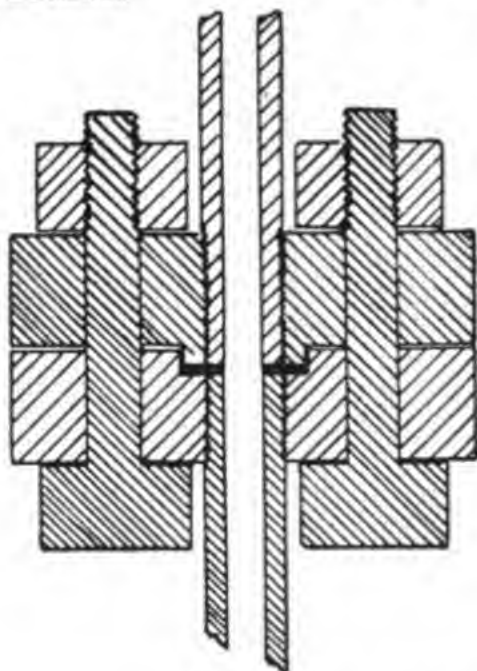


FIG. 123.

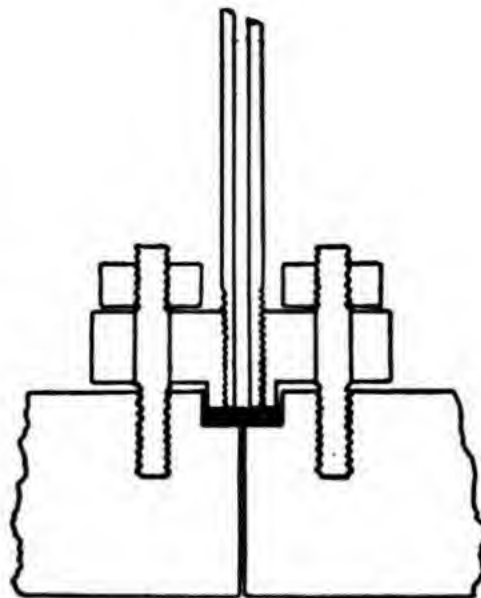


FIG. 124.

(From *Chem. and Ind. (J.S.C.I.)*, May 28, 1926, 367)

5232. In making joints between a high-pressure vessel and its tubular connections, or between two lengths of such connections, rotating jointing faces should be avoided. For

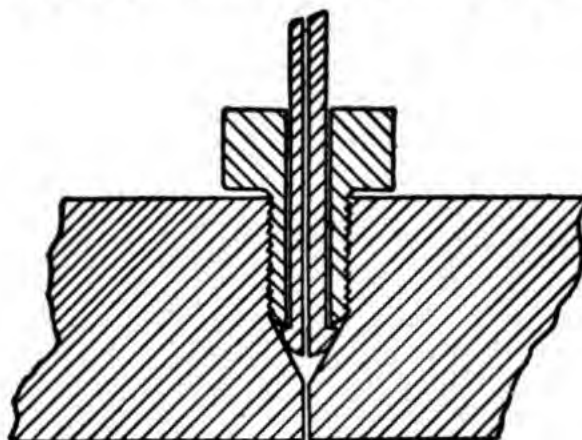


FIG. 125.

connections at a metal face a metal-to-metal ball and cone joint of the type used on cylinders for holding compressed gas is satisfactory (Fig. 125). No jointing ring is employed and,

the ball joint being only loosely coupled to the screwed-down part, no rotation of the ball face takes place during the tightening.

5233. Sliding Joints. The leather bucket type of sliding joint seems to be the only one which has proved satisfactory under high pressure. A simple form of such a joint is shown in Fig. 126.

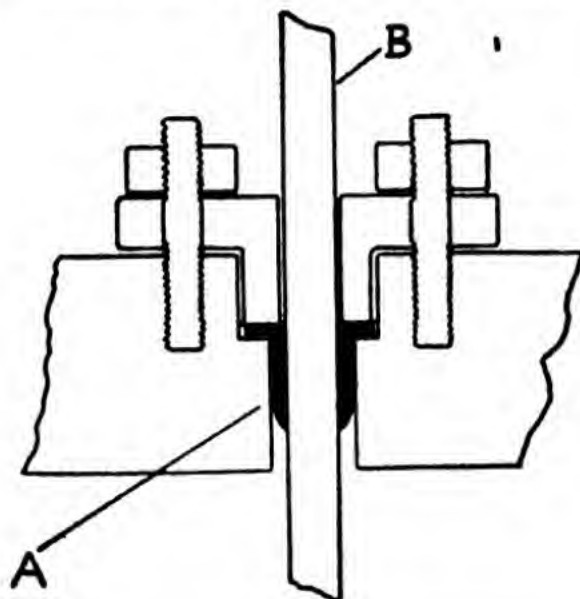


FIG. 126.

5234. Electric Leads. Electric leads for heating, pyrometer wires and the like have frequently to be run through the walls of high-pressure vessels. Figure 127 shows a simple method of passing an electric lead. A is the bolt for carrying the current; B₁ and B₂ are insulating gaskets of vulcanized fiber; C is a steel gasket to protect the outer fiber gasket. An insulating tube, shorter than the thickness of the vessel wall lines the drilled hole through

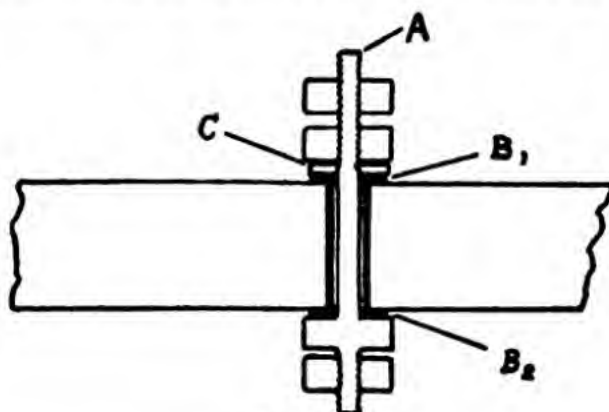


FIG. 127.

which the conducting bolt passes. Figure 129 shows a method of effecting the same thing without the use of vulcanized fiber and which, therefore, will allow of exposure to higher temperatures. It is used where the space in the head is small. The insulating material is "selected" soapstone, i.e., soapstone whose faces are either parallel to or at right angles to the cleavage planes. The contained angles of the truncated cones are cut to a little under 60°

—about 58° – 59° , the seat and follower ring are cut to 60° . If the vessel has to be tested hydraulically, the soapstone must not be in place and the hole must be plugged, as soapstone will not stand up against water under pressure. It will, however, stand oil pressure.

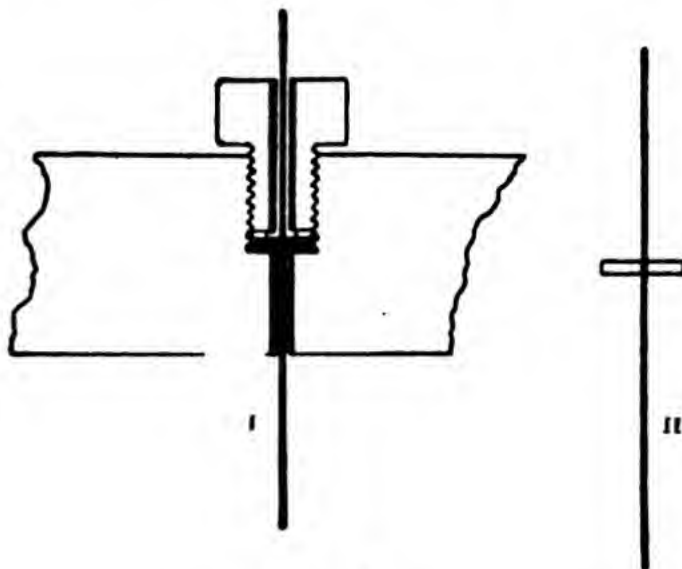


FIG. 128.

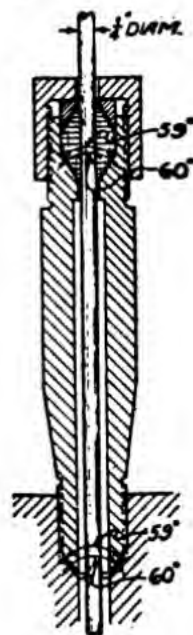


FIG. 129.

5235. Ernst and Reed ²³ give a detailed description of a high-pressure relief valve which has the advantage over a pop valve that it reseats itself after relief of the excess pressure. A section of this valve is also shown in Ernst's article in *Ind. Eng. Chem.*, 1926, **18**, 668.

5236. Larson and Karrer ²⁴ figure and describe a magnetic regulating valve for maintaining constant pressure in a high-pressure system. It is intended, primarily, for use where the gas under pressure is supplied from storage cylinders.²⁵

5237. Ramsey ²⁶ gives a summary review of high-pressure equipment.

EXPERIMENTAL HIGH-PRESSURE WORK IN GAS PHASE

5238. The methods used in high-pressure experimental work are well exemplified in the small-scale synthesis of methanol from carbon monoxide and hydrogen.

5239. Typical apparatus and methods are described in the following articles: Lewis and Frolich: Synthesis of methanol from carbon monoxide and hydrogen, *Ind. Eng. Chem.*, 1928, **20**, 285; Frolich, Fenske and Quiggle: Decomposition of methanol by catalysts composed of copper and zinc, *Ind. Eng. Chem.*, 1928, **20**, 694; Morgan, Taylor and Hedley: Syntheses under high pressure—interaction of carbon monoxide and hydrogen, *J.S.C.I.*, 1928, **47**, 117T; Krase: High-pressure gas research at the University of Illinois, *Chem. Met. Eng.*, 1928, **35**, 463; Brown and Galloway: Methanol from hydrogen and carbon monoxide, *Ind. Eng.*

²³ *Mech. Eng.*, 1926, **48**, 595.

²⁴ *Ind. Eng. Chem.*, 1922, **14**, 1012.

²⁵ Diagram and short description in Ernst, *Ind. Eng. Chem.*, 1926, **18**, 668.

²⁶ Chemical engineering in high-pressure processes. *Ind. Chemist*, 1927, **3** 391; *Chem. Abst.*, 1928, **22**, 126. Corblin describes means for removing and measuring liquids from containers containing gases under high pressure, such as methanol or ammonia from catalytic apparatus in which they are formed. French Pat. 660,353, Dec. 24, 1927; *Chem. Abst.*, 1930, 175.

Chem., 1928, **20**, 960. The Fixed Nitrogen Research Laboratory of the Bureau of Chemistry and Soil, U. S. Department of Agriculture, has published a bulletin descriptive of satisfactory equipment for high-pressure laboratory work, up to 1500 atmospheres. This includes working drawings of almost all machine work necessary.²⁷ Hopkins, *Times Trade and Eng. Suppl.* (London), 1928, **23**, 34.

5240. Provision must be made for the following: 1. Preparation, purification, and storage of carbon monoxide. 2. Compression and temporary storage of mixed gases. 3. Reaction tube (static or flow) with means for determining temperature and for controlling the same. 4. Condensing apparatus. 5. Recirculation circuit. 6. Guard screen.

5241. Preparation of Carbon Monoxide. Carbon monoxide is produced by heating together formic and sulphuric acids. The reaction takes place in two "tantiron" vessels (Fig. 130), which are half-filled with sulphuric acid, heated to

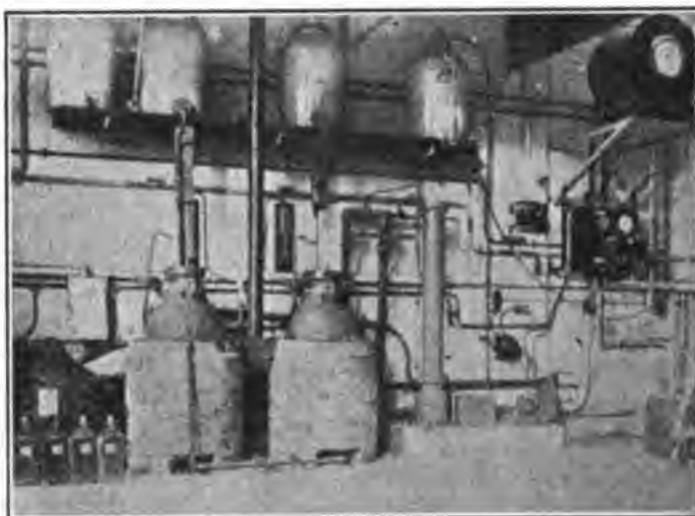


FIG. 130.

about 200° by gas ring burners. Formic acid, stored in earthenware jars overhead, is delivered slowly through a tube dipping below the surface of sulphuric acid, when carbon monoxide is evolved in a steady stream. This gas, after washing in a tower packed with broken silica ware, down which flows 10 per cent aqueous caustic soda, is collected in a gas-holder. The water produced in the reaction is evolved as steam which condenses at the base of the caustic soda tower; there is therefore no dilution of sulphuric acid, which may be used almost indefinitely. The iron vessel appears to be only slightly corroded, while the carbon monoxide produced contains less than 0.5 per cent of hydrogen.²⁸ Brown and Galloway (*loc. cit.*) use phosphoric instead of sulphuric acid and wash the gas with water and alkali.

5241A. Pure Carbon Monoxide for Experimental Purposes. Thompson

²⁷ Dille. A High-pressure Gas-compression System, U. S. Dept. of Agriculture, Circular No. 61, Jan., 1929, 18 pages with many illustrations and cost estimates.

²⁸ Morgan, *et al.*, *loc. cit.*

describes an apparatus in which carbon monoxide of 99.9 per cent purity can be prepared. A regulated stream of formic acid is dropped into 85 per cent phosphoric acid heated at 170°. The water vapor and unchanged formic acid are condensed from the gas stream, which is then washed with dilute sodium hydroxide solution. After compressing into steel cylinders traces of iron carbonyl and carbon dioxide were found in the gas. The combined output of two generators (10-liter Pyrex flasks) is 200 cu. ft. in 7 hrs. with an efficient utilization of formic acid of 92 per cent. The phosphoric acid baths can be used indefinitely.^{28a}

5242. Commercial hydrogen in cylinders ordinarily is used.²⁹ A convenient and inexpensive laboratory apparatus for the electrolytic preparation of hydrogen is described by Fink and Mantell.³⁰ This is a simple glass cell using nickel electrodes in a 30 per cent sodium hydroxide solution. At 15 amperes 5.66 liters per hour of hydrogen are produced.

5243. Storage of the carbon monoxide requires only gas holders of the familiar inverted bell type with water seal and counterpoise. Before passing to the compressor, the gas may be sent through a train of scrubbers.

5244. Compression. Up to the ordinary pressures of the methanol synthesis, with a maximum of 4000 lb. to the square inch (275 atmospheres) compression of the mixed gases may be carried out by three-stage water-cooled compressors,³¹ of which several makes are on the market. For higher pressures, on a laboratory scale, hydraulic compression seems, at present, the only means available.³² The first experiments of Morgan and his collaborators were carried out with the aid of a hydraulic compressor system, constructed from units supplied by the British Oxygen Company.

5244A. The apparatus (Figs. 131 and 132) consists of cylinders, H_1 , H_2 , $\frac{1}{2}$ cu. ft. capacity, designed to work up to 300 atmospheres; each cylinder is provided with a water reservoir, R_1 , R_2 , from which water can be pumped into the cylinder, or into which water can be returned from the corresponding cylinder. These cylinders are first filled with compressed gas from the storage cylinder (C_1 -4), which is then further compressed by pumping in water. In each reservoir a float actuates an alarm when the corresponding cylinder is either nearly full or nearly empty. The tubing used to carry the compressed gas, tested to 400 atmospheres, is made of soft, solid-drawn copper, $\frac{1}{8}$ in. internal diameter, $\frac{1}{4}$ in. external diameter, or $\frac{1}{4}$ in. internal diameter and $\frac{1}{2}$ in. external diameter. Steel tubing $\frac{1}{8}$ in. internal diameter and $\frac{1}{2}$ in. external diameter is used when the temperature does not permit of the use of copper.

A joint is made between two pieces of the small-size tubing by means of a close-fitting sleeve, the joint being finally sealed by soft solder, or silver solder, according to the temperature to be attained by the joint. The sleeve is made a "push fit" to keep the film of solder as thin as possible. T-pieces, elbow joints, and sockets (Fig. 133) are made of mild steel turned up from the solid and bored for a "push in" fit, secured by soldering. The surfaces of joints before soldering are tinned when possible. In the case of the larger size of copper tubing, it is found necessary to screw all joints before soldering. Unions of the ball-and-socket type, made of drawn brass, have proved effective when there is no great temperature

^{28a} *Ind. Eng. Chem.*, 1929, **21**, 389; *Brit. Chem. Abst.*, 1929, 431B.

²⁹ " . . . electrolytic hydrogen from the manufacturer whose product was used in these experiments has since been found to be contaminated occasionally with illuminating gas." Lewis and Frolich (*loc. cit.*).

³⁰ *Trans. Am. Electrochem. Soc.*, 1927, **52**; *Chem. Abst.*, 1927, **21**, 2849.

³¹ Krase, *loc. cit.*

³² Krase, *loc. cit.*; a Reavell compressor, compressing 3 cu. ft. per min. to 300 atmospheres, was used by Morgan and his collaborators.

change. The union between valves and tubing is made with an annular knife edge, integral with the bronze valve casting, which is seated on a soft copper disc brazed on the tube end.

The smaller size valve³³ consists of a steel spindle tapering to a point, which closes down on a bronze seat integral with the body. The screwed portion of the valve spindle lies between the tapered point and the gland packing. In the larger type the valve itself is free to rotate in a brass bush screwed into the spindle; there is, consequently, no grinding action between the valve and its seating when brought into contact.³⁴

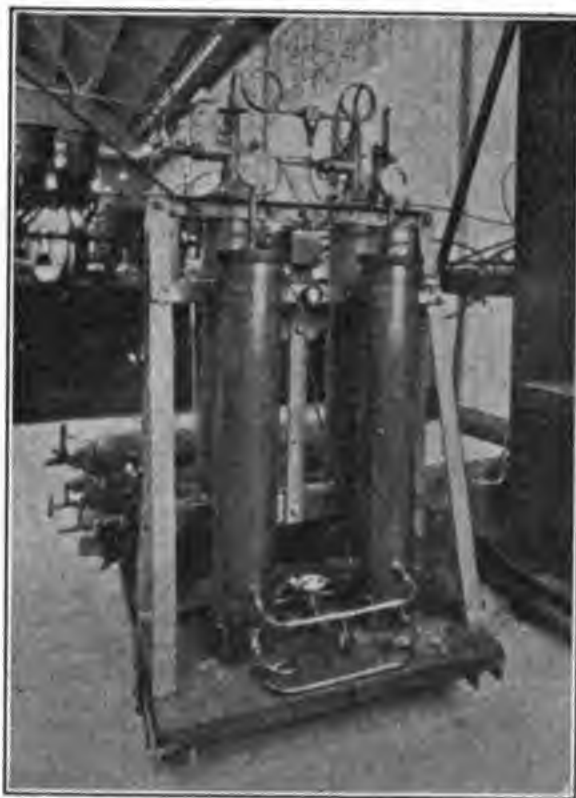


FIG. 131.

5245. Hydraulic pumps for pressures even above 100 atmospheres are available commercially. Ernst (*loc. cit.*) describes and illustrates such a pump made and used at the Fixed Nitrogen Research Laboratory.

5246. Bourdon gauges having proved unreliable (breaking at pressures below those for which they were supplied) Ernst (*loc. cit.*) illustrates and describes a dead-weight gauge which has given satisfaction.

5247. The gases compressed to the desired degree are stored in cylinders of the usual type, provided with the necessary valves. From these the gas is delivered to the reaction vessel. It is an occasional practice to place an oil-separator and purifiers between the storage cylinder and the catalyst-containing reaction vessel.³⁵ Also there may be advantage in pre-heating the gas.³⁶ When first intro-

³³ Valves supplied by British Oxygen Co.

³⁴ Morgan, Taylor and Hedley, *loc. cit.*

³⁵ Lewis and Frolich, *loc. cit.*

³⁶ Brown and Galloway, *loc. cit.*

duced gas may advantageously be passed over heated copper oxide and through calcium chloride and soda lime. In this way oxygen, water and carbon dioxide

are removed and also, it seems,³⁷ any iron carbonyl that may be present.

5248. The Reaction Vessel (Catalyst Tube). The design of the vessel in which the reactant gases are to be brought in contact with the catalyst depends on whether the operation is to be "static" or "flow" in character. In the static type the gases are sealed with the catalyst under a high initial pressure, which falls as the reaction proceeds, the fall being observed on a gauge. In the flow type the gases are caused to pass continuously over the catalyst, generally with recirculation, sometimes with the addition of make-up gas, and always with removal of reaction products.

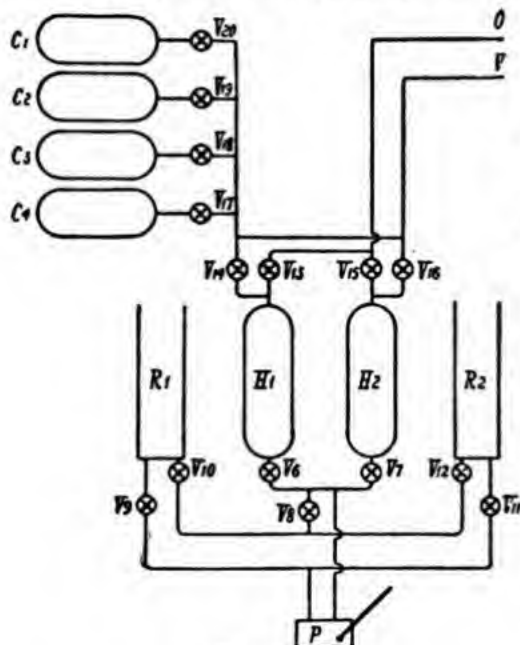


FIG. 132.

lysts consisted of a copper-lined steel reaction vessel *A* (Fig. 134), heated in a metal bath *E*. An immersed thermo-couple, *TC*, indicated the temperature. The compressed gas mixture was led quickly through the valves *V*₁ and *V*₂ into the reaction vessel which held the catalyst. As soon as the required pressure (say 200 atmospheres) was reached the valve *V*₂ was closed,

5249. Static or Bomb Apparatus. The apparatus first used by Morgan for testing cata-



FIG. 133.

and the time taken for the pressure, as shown by the gauge *B*, to fall a given number of atmospheres. After an experiment the gases were led to waste through valve *V*₄. The apparatus was mounted in an angle-iron frame behind the steel-plate screen, which carried in front the control valves, Budenberg pressure gauges (no-capacity type), and pyrometer indicator. A section of the reaction vessel (Fig. 135) shows that the actual joint was made

³⁷ Brown and Galloway, *loc. cit.*, quoting Fieldner and Jones.

between a phosphor-bronze cap, brazed on to the copper inlet tube, and the lip of the copper liner; graphite composition was placed on the two surfaces to prevent welding together under conditions of high pressure and temperature. The apparatus was tested for leaks before an experiment by filling with compressed hydrogen, when any diminution of pressure after the catalyst had been reduced could only be due to leakage.

5250. Flow Apparatus. Krase uses a 1-in. O.D. by $\frac{3}{4}$ -in. I.D. nichrome tube internally copper-plated. He does not give the length, but states that a quantity of catalyst which has a bulk of 15 cc. is normal and permits of due flow of the gases. An aluminum sleeve is cast around the tube for about 1 ft. of its length: this is to insure uniformity of temperature. Heating is effected by a split, multiple-unit electric furnace, controlled by a rheostat. The

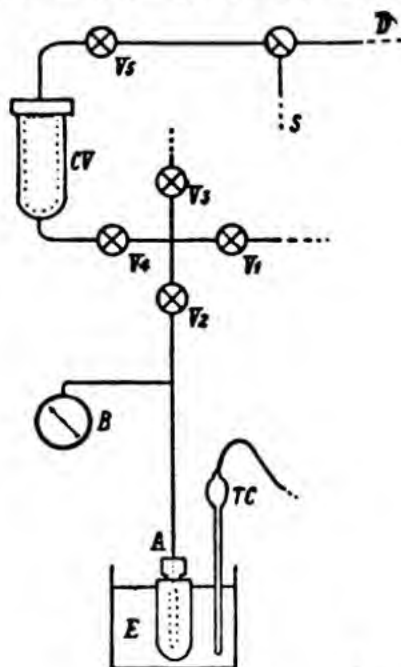


FIG. 134.

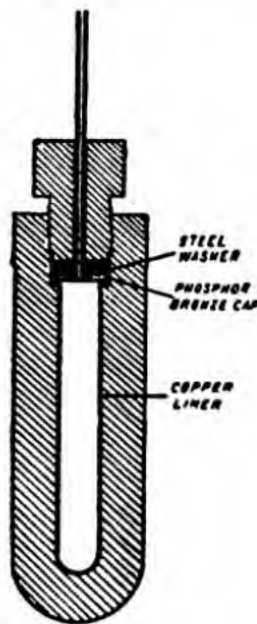


FIG. 135.

temperature of the catalyst is estimated by observation of the temperature of the aluminum sleeve and by applying the observed average difference between the temperature of the two tubes. The tubes used by Lewis and Frolich were constructed of chrome vanadium steel, copper-lined. They were fitted with thermocouple wells. The catalyst occupied one-third of the free space, the lower and upper parts being filled with copper shot to insure uniformity of temperature. The first, small, flow apparatus used at Teddington (Morgan, Taylor and Hedley) had a reaction vessel of Vibrac steel, copper-lined, the end pieces being constructed as for the static bomb already described. This was heated in a metal bath. In their larger plant three copper-lined steel reaction vessels, each of 70-cc. capacity, were placed vertically in a metal bath heated by a gas ring. The metal bath was kept at a uniform temperature by means of a mechanical stirrer.

5251. Condensing System. The reaction vessel leads to a water-cooled spiral condenser and receiver. In the Teddington apparatus the union between the reaction vessel and the condenser is water-cooled to prevent loosening of the joints from undue temperature variation. Blocks of copper fitted to each of the delivery pipes between the reaction vessel and the water-cooled union are drilled for thermometers: the temperature of the block is an indication of the rate of flow of gas. The three reaction vessels may be used in series or in parallel. The receiver is fitted with a valve for the withdrawal of condensate: this valve is in front of the control panel.

5252. Circulating System. The gas is forced round the system by a circulating pump fitted with an oil separator. It was found necessary²⁸ to place in this part of the circuit

²⁸ Both at Teddington and at the U. S. Bureau of Mines Station (Brown and Galloway).

an auxiliary condenser cooled to a lower temperature than the main condenser. The object of this was to prevent alcohol separating with the oil. The circulating pump used at Teddington is of the double-acting type, designed to pass 120 cc. of compressed gas each complete revolution. The volume displaced by the piston at each end of the cylinder is identical, since the piston rod passes right through the cylinder and glands are fitted at each end. The latter are sealed with oil supplied under pressure from a small force pump driven by an eccentric on the crank shaft. The gland packing, originally of the standard hydraulic hat leather type,³⁹ has since been replaced by standard S.E.A. rings. The present packing, which is still in use, has functioned without adjustment in more than two million revolutions, a performance corresponding with fifty working days of twenty-four hours each. Provision should be made for taking samples of the circulating gases. This can best be done by placing a sampling valve on a holder in the recirculation circuit. This valve should deliver in front of the control panel. The tubing throughout should be of copper and the pumps are, preferably, made of bronze.

5253. Control Panel. The operator should be able to manipulate all valves, take samples and read gauges while separated by a safety screen from the high-pressure cylinders, etc. At the University of Illinois (Krase, *loc. cit.*) the storage cylinders, gauge and valves are shielded from the main laboratory by a three-sided steel structure, open at the top and rear. Extension handles enable the valves to be operated from the "safe" side of this screen.

5254. Apparatus for Decomposition of Methanol. One research of Frolich, Fenske and Quiggle⁴⁰ was concerned, not with the catalytic synthesis of methanol from carbon monoxide and hydrogen, but with the catalytic decomposition of methanol into carbon monoxide and hydrogen. It was therefore carried out at atmospheric pressure.⁴¹ Nevertheless, it was directly relevant to our subject because its object was the investigation of catalysts suitable for the methanol synthesis. It was "justifiable to suppose that the catalyst mixture giving the maximum decomposition into carbon dioxide and hydrogen would be particularly suitable for the synthesis of methanol from these same gases under pressure. Indeed, the early researches of Sabatier⁴² served as a guide in the search for catalysts for the methanol synthesis."⁴³

5255. The results of this research are mentioned elsewhere: we are here concerned with the apparatus and method. Referring to Fig. 136, *A* is a graduated 10-cc. bulb containing methanol heated by boiling carbon tetrachloride (b.p. 76° C.) in the 1-liter wide-mouthed Erlenmeyer flask, *B*, provided with a reflux condenser, *C*. The funnel, *D*, supplies a means of introducing methanol into the bulb, *A*, through the stopcock, *E*. The methanol vapor generated in *A* under pressure (because the carbon tetrachloride boils 11° C. above the normal boiling-point of the alcohol) passes at a constant rate through the electrically heated orifice, *F*, and the stopcock, *H*, into the reactor, *I*. The orifice line also has a side arm, *G*, through which nitrogen may be introduced for flushing out the system. The reactor, *I*, consists of a 16 by 250-mm. Pyrex glass tube fitted snugly into another of 20 mm. diameter and wound with chromel ribbon for electrically heating the chamber. A 35-mm. Pyrex glass tube encloses the reactor and enables satisfactory temperature control. A calibrated thermometer, *K*, fitted into the reactor by means of an asbestos plug, the joint being made gas-tight by litharge-glycerol cement, projects into the reactor as far as the catalyst, which is located in a 12 by 88-mm. porcelain boat in the center of the reaction chamber.

³⁹ Ronald Trist, London.

⁴⁰ *Ind. Eng. Chem.*, 1928, **20**, 694; cf. para. 1311.

⁴¹ CH_3OH (1 vol.) \rightarrow CO (1 vol.) + 2H_2 (2 vols.): the reaction resulting in an increase of volume is favored by low pressure. Frolich, Fenske, Taylor and Southwick (*Ind. Eng. Chem.*, 1928, **20**, 1327; *Brit. Chem. Abst.*, 1929, 153A), synthesizing methanol, demonstrated the justice of their reasoning.

⁴² Sabatier and Mailhe, *Compt. rend.*, 1908, **146**, 1376; 1909, **148**, 1734; Sabatier and Senderens, *ibid.*, 1903, **136**, 921.

⁴³ See Lormand (on Patart's work), *Ind. Eng. Chem.*, 1925, **17**, 430.

The boat is introduced and removed at the left-hand end of the chamber. The reaction gases and undecomposed methanol leave the reactor through the exit tube, *L*, the gas passing through three low-head scrubbers, *M*, in series, the first containing distilled water, the second a mixture of 50 per cent pure methanol and 50 per cent distilled water, and the third pure methanol. The undecomposed methanol condenses in the first scrubber. The reaction gases pass through a fourth scrubber, a Kunz absorption bulb, which contains pure methanol and is immersed in a mixture of carbon dioxide snow and ether (temperature $-76^{\circ}\text{C}.$) in a Dewar flask, *N*. The reaction gases are then collected over a saturated zinc sulphate solution in the 4-liter gasometer, *O*, provided with a manometer, *P*, and a leveling device, *Q*.

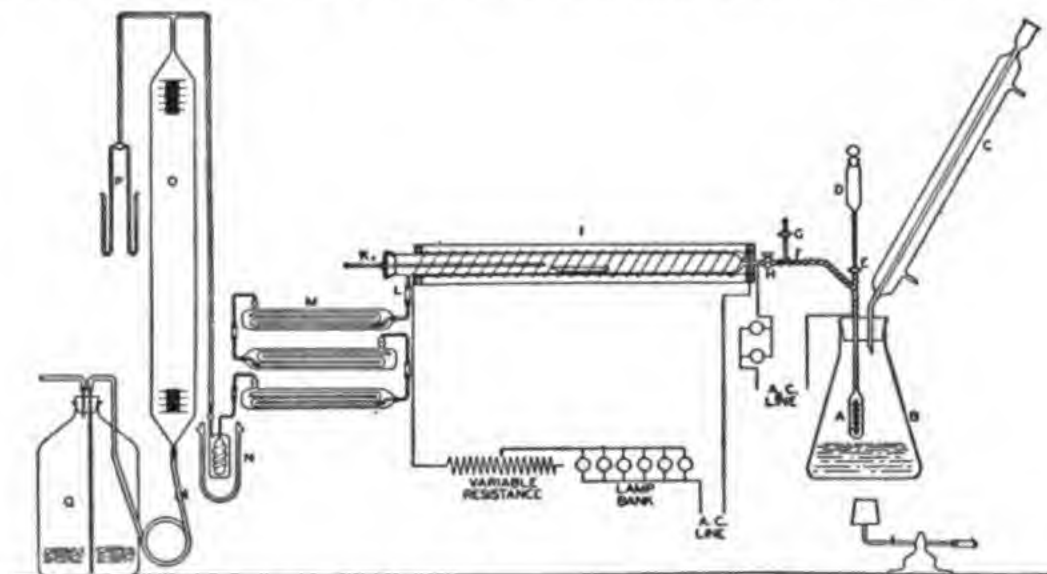


FIG. 136.—APPARATUS USED BY FROLICH, FENSKE AND QUIGGLE IN STUDYING THE DECOMPOSITION OF METHANOL. See paragraph 5255.

5256. Procedure. Before each run the entire system is flushed out with nitrogen. Without collecting any reaction products, .0462 mol of methanol is passed over 0.43 g. of catalyst for reduction, the temperature being kept as low as possible that the most active catalyst may be obtained. Then, with the system in readiness to collect the decomposition products, 0.1156 mol of methanol is passed at a constant rate over this catalyst in ninety-three minutes. In every run the temperature is $360^{\circ}\text{C}.$ and the total pressure 1 atmosphere (plus a head of liquid in the scrubbers which is always between 6 and 7 mm. of mercury). The undecomposed methanol, as well as the methyl formate and formaldehyde formed, is taken out in the scrubbers, *M*, any last traces of the last two products being caught in the low-temperature scrubber, *N*. The reaction gases pass on and are collected in the gasometer, *O*. At the end of the run, when 0.1156 mol of methanol has passed over the catalyst, the residual decomposition products are swept into the gasometer with nitrogen. Before the catalyst is removed it is cooled to room temperature by a constant stream of nitrogen in order to prevent oxidation and permit further study of its chemical composition and physical structure. The reaction gases are analyzed in a Burrell gas-analysis apparatus for carbon dioxide, unsaturateds, oxygen, hydrogen, carbon monoxide, and methane. Formaldehyde is determined by the iodine method: methyl formate by adding excess of 0.1 *N* sodium hydroxide and, after standing, titrating the excess sodium hydroxide.

5256A. Investigations of a similar character have been made by Huffman and Dodge. Experiments were carried out at 350° with catalysts varying in composition from pure zinc oxide to pure chromic oxide.^{43a} The catalysts were

^{43a} Huffman and Dodge, *Ind. Eng. Chem*, 1929, **21**, 1056.

prepared by precipitation of the hydroxides from solutions of the mixed nitrates by addition of ammonia solution. After washing and drying at 110° , the catalysts were reduced by hydrogen up to a temperature of 300° before being used. The addition of a small amount of chromium oxide to zinc oxide caused a decrease in the total decomposition of methyl alcohol, contrary to its effect in the synthesis. If only the decomposition into carbon monoxide and hydrogen is considered the effect is in accord with that observed in the synthesis. In all the decomposition

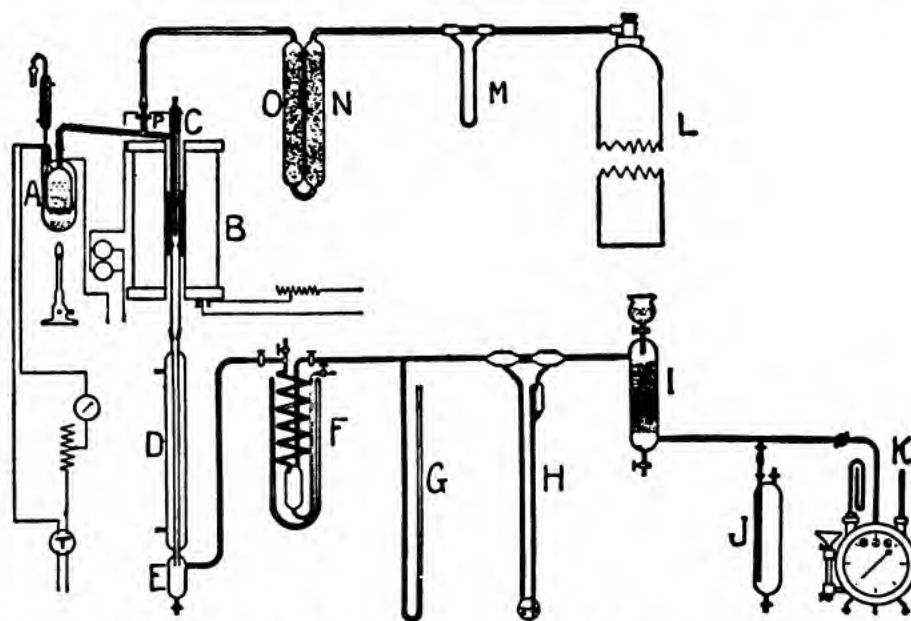


FIG. 137.—APPARATUS USED BY HUFFMAN AND DODGE IN OBSERVATIONS ON THE DECOMPOSITION AND SYNTHESIS OF METHANOL, EMPLOYING AS CATALYSTS VARIOUS MIXTURES OF OXIDES OF ZINC AND CHROMIUM.

A, an "adiabatic" boiler; B and C, catalyst chamber; D, condenser; F, freezing coil condenser; G, manometer; H, flowmeter; I, water scrubbing column; J, sampler; K, gas meter; L, hydrogen cylinder; M, flowmeter; N and O, purifiers. The experimental method consisted in passing methanol vapor at a constant rate of 0.00970 g. per second through a bed of granular catalyst supported in a vertical glass tube and heated by an electric furnace to a constant temperature of 350° C. The liquid and gaseous products leaving the catalyst were collected and analyzed to determine the nature and extent of the decomposition. The rate of passage of methanol vapor was so chosen that the maximum decomposition obtained with the best catalyst was considerably less than 100 per cent in order to compare the activity of the catalysts at a point sufficiently removed from equilibrium. *Ind. Eng. Chem.*, 1929, **21**, 1056.

experiments the activity of the catalysts was found to decrease. No such decrease was observed in the synthesis experiments. In addition to carbon monoxide and hydrogen the following substances were detected during the decomposition: carbon dioxide, methane, methyl formate, formaldehyde, dimethyl ether, unsaturated compounds, together with traces of unidentified substances. The percentage of methyl alcohol decomposed into various products is expressed as a function of the composition of the catalyst. Although the results obtained differ in some respects from those of Frolich and his co-workers, the catalyst

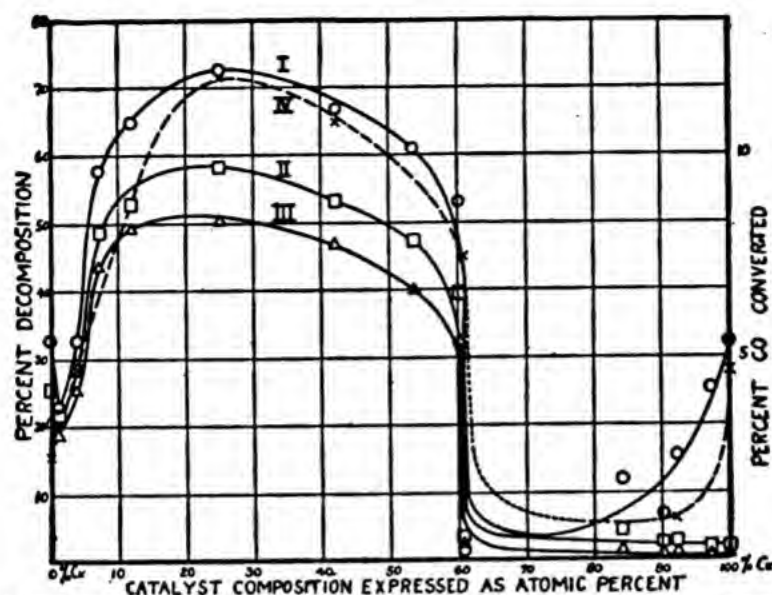


FIG. 138.—PERCENTAGE DECOMPOSITION AS A FUNCTION OF CATALYST COMPOSITION AND COMPARISON OF SYNTHESIS AND DECOMPOSITION RESULTS WITH THE SAME CATALYSTS.

Curve I—Total percentage methanol decomposed; Curve II—Percentage methanol decomposed as based on free hydrogen in gas; Curve III—Percentage methanol decomposed as based on carbon monoxide in gas; Curve IV—Percentage carbon monoxide converted in the synthesis. Huffman and Dodge, *Ind. Eng. Chem.*, 1929, **21**, 1056.

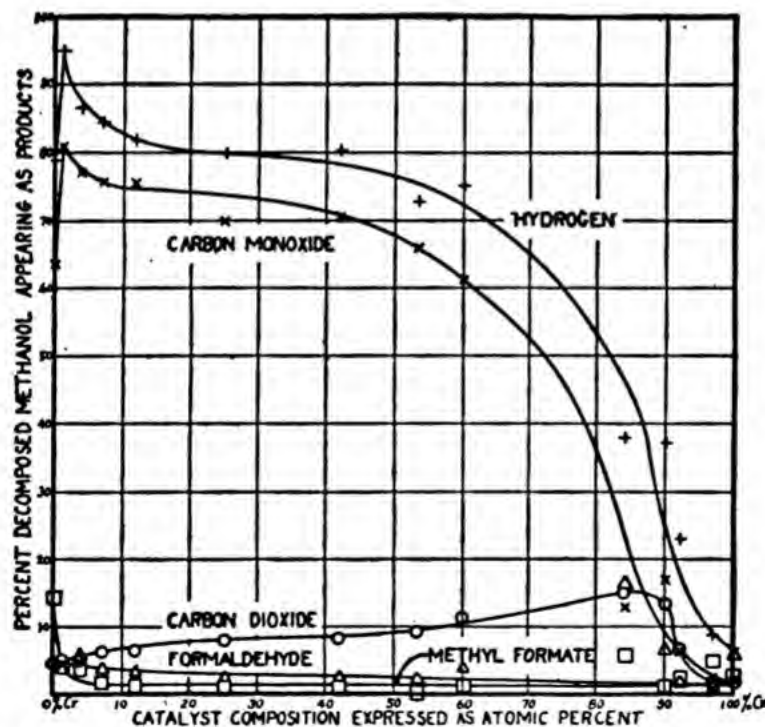


FIG. 139.—PERCENTAGE OF THE DECOMPOSED METHANOL WHICH APPEARS AS VARIOUS PRODUCTS AS A FUNCTION OF CATALYST COMPOSITION. Huffman and Dodge, *Ind. Eng. Chem.*, 1929, **21**, 1056.

having the maximum activity was found to have the composition $\text{Zn/Cr} = 4$, in close agreement with Frolich's work. See Figs. 137, 138, 139, and 140.

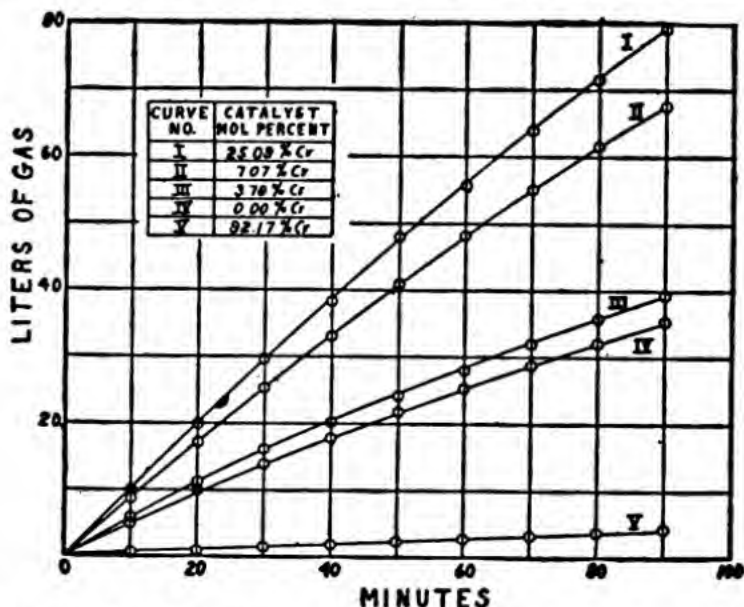


FIG. 140.—RATE OF GAS PRODUCTION WITH VARIOUS CATALYSTS. Huffman and Dodge, *Ind. Eng. Chem.*, 1929, **21**, 1056.

HIGH-PRESSURE WORK IN THE GAS PHASE CATALYSTS

5257. Catalysts Used in Experimental Work. It is of interest to note what catalysts were used by the experimenters whose apparatus and methods we have been considering, how they were prepared, and the results obtained.

5258. The most notable thing is that none of these groups of workers reports experiments in which zinc was absent from the catalyst. Nor does any one of them appear to have worked with catalysts containing iron, nickel or cobalt.⁴⁴

5259. While a number of qualitatively different catalysts were tested (especially by Morgan and his collaborators at Teddington) it is significant that, for the main experiments, three of the groups used catalysts containing compounds of zinc and copper, in one case as chromates. The fourth group used chromates of zinc.

5260. Zinc Oxide Alone. Because Sabatier had found zinc oxide alone to be a good catalyst for the decomposition of methanol, Patart⁴⁵ turned to it first in his search for a synthetic catalyst. He was disappointed, however, and, damning it with faint praise, turned to and had better results with mixed oxides. That methanol can be obtained with this catalyst, but that it is of low activity was also the conclusion of the Teddington workers.⁴⁶ The zinc oxide catalyst they used was made by mixing the oxide with water to a thick paste, squeezing this through a circular orifice, drying the vermiform mass thus obtained at 130° C., breaking up into granules, and using those which would pass through a sieve with circular holes 0.5 cm. diameter and not through one with holes 0.25 cm. diameter.

⁴⁴ The reference is to methanol synthesis only.

⁴⁵ *Bull. soc. d'encour.*, 1925, **137**, 141.

⁴⁶ Morgan, Taylor and Hedley, *loc. cit.*; also Frolich *et al.*, *loc. cit.*

5261. The most elaborate study of the behavior of the zinc oxide catalyst is that recorded by Brown and Galloway.⁴⁷ They prepared the catalyst by precipitating basic zinc carbonate from hot solutions of zinc nitrate and sodium carbonate and washing it free from nitrates. The moist precipitate was pressed into threads 2.4 mm. diameter, air-dried and then slowly heated up to 300° C. under reduced pressure. The resulting oxide was used directly. It was found to be less efficient than the other catalysts (normal and basic zinc chromates) in that it was less active, gave poor yields at low temperatures and was shorter lived. The details will be taken up in a later part of this chapter.

5262. Highly Active Zinc Oxide Catalyst.⁴⁸ According to British Celanese, Ltd., Bader and Green, a zinc oxide catalyst for methanol synthesis may be prepared which is highly active without a promoter, such as chromium oxide, and which is not usefully improved by the addition of a promoter. Zinc carbonate is precipitated from a very dilute solution in presence of protective colloids such as starch, saponin, pectin, hydrated silica. Electrolytes are removed by thorough washing and the zinc carbonate gel is dried by heating under reduced pressure. The conversion to oxide by heating must be carried out at temperatures between 250° and 400° C.

5263. Zinc Oxide and Copper Oxide. This mixture was tried by Morgan and his collaborators and it was the catalyst used by Frolich, Fenske and Quiggle, as well as by Lewis and Frolich, in the last case with an admixture of alumina. The article by the first group merely mentions the trial of this mixture without further particulars as to proportions, mode of preparation, or results.

5264. Frolich, Fenske and Quiggle describe the preparation of catalyst as follows: Ammonia was added to 1 mol of a mixture of chemically pure zinc and copper nitrates dissolved in 3 liters of distilled water. The solution was kept at a constant temperature of 85° C. and thoroughly agitated by a motor-driven stirrer. Ammonia, 1 part by volume of concentrated chemically pure ammonia of specific gravity 0.89 to 2 parts of distilled water, was added at a constant rate of 20 cc. per minute until the end-point was reached, zinc and copper hydroxides being precipitated together.

5264A. Unless the precipitates settled immediately, in which case they were washed by decantation, the suspensions were poured onto a suction filter, the unfiltered portions being kept at 85° C. until ready for filtering. The precipitates were then washed with 8 liters of distilled water at 85° C., the precipitates on the filter being stirred as much as possible. When the hydroxides became caked on the filter, they were removed and dried for three days in an oven at 110° C. After crushing and screening through a 60-mesh sieve, the catalysts were heated for four hours at 220° C., the hydroxides being converted to the oxides and any adhering ammonium salts volatilized and driven off by a constant stream of nitrogen passing through the heating chamber.

5264B. The catalysts were analyzed for copper by dissolving 0.2 to 0.4 g. of the oxides in 6 *N* sulphuric acid, cooling, adding potassium iodide, and titrating with 0.1 *N* thiosulphate solution. From these data the per cent copper oxide was calculated, the per cent zinc oxide being determined by difference.

5264C. The method of precipitating zinc and copper hydroxides together was chosen because experiments on catalysts prepared (1) by precipitating zinc hydroxide on copper hydroxide, (2) by precipitating copper hydroxide on zinc hydroxide, (3) by mixing the hydroxide gels, and (4) by calcining the nitrates showed the resulting mixtures to be inferior in activity to the catalysts made by precipitating the hydroxides together.

COMPARATIVE EFFICIENCY OF COPPER OXIDE-ZINC OXIDE CATALYSTS ⁴⁹ PREPARED BY VARIOUS METHODS

Method of Preparation	Decomposition Efficiency
Zinc hydroxide precipitated on suspended copper hydroxide....	75
Copper hydroxide precipitated on suspended zinc hydroxide.....	67
Hydroxide gels mixed.....	83
Calcined nitrates.....	70
Co-precipitation of hydroxides.....	100

⁴⁷ *Loc. cit.*

⁴⁸ Brit. Pat. 300,142, May 2, 1927, to British Celanese, Ltd., Bader and Green.

⁴⁹ Composition of catalyst: copper oxide, 95 mol per cent; zinc oxide, 5 mol per cent.

5264D. The catalyst prepared by co-precipitation of the hydroxides showed a definite superiority over those made by other methods. Therefore extended work was done with such catalysts to determine the effects of variations in the proportions of the two constituents. Bearing in mind that we are dealing with the efficacy of the catalysts for decomposition, the results are summarized as follows: 1. The maximum decomposition of methanol and formation of carbon monoxide occur when the zinc oxide is present in excess. 2. Between 40 and 50 mols per cent zinc oxide, the mols of carbon monoxide formed per mol of methanol increase about 350 per cent. 3. The addition of a small amount of zinc oxide to copper oxide markedly increases the decomposition of methanol. A catalyst composed of 3 mol per cent zinc oxide and 97 mol per cent copper oxide decomposes 26 per cent of the methanol, while pure copper decomposes only 9 per cent under otherwise constant conditions. 4. A similar promoter effect is observed when a small amount of copper oxide is added to zinc oxide. That is, a mixture containing 98.6 mol per cent zinc oxide and 1.4 mol per cent copper oxide decomposes 41 per cent of the methanol, whereas pure zinc oxide decomposes 33 per cent under parallel conditions. 5. Copper promoted with zinc oxide especially favors the formation of methyl formate, while carbon monoxide formation is favored by zinc oxide promoted with copper.⁵⁰

5265. Catalytic Decomposition of Methanol. Applying the results obtained in the work on the catalytic decomposition of methanol, Frolich, Fenske, Taylor and Southwick have used the copper oxide—zinc oxide catalysts in methanol synthesis at 204 atmospheres. They conclude that the atmospheric pressure decomposition method of testing is applicable for the selection of catalysts for the methanol synthesis at high pressure.

5266. The reversal of the methanol synthesis—the catalytic decomposition of methanol into carbon monoxide and hydrogen—has also been studied by Smith and Hawk.⁵¹ The temperatures were about 300° C., the catalysts similar to those used in the synthesis: zinc oxide, zinc oxide with chromic or vanadic acid, cadmium oxide and chromic acid. The analogous decomposition of formic acid was investigated by Müller and Schwabe,⁵² using as catalysts the metals of the platinum group prepared by the method of Paal and Poethke. Of these palladium was by far the most active: platinum was less active, the others inactive.

5267. The catalyst used by Lewis and Frolich had an original⁵³ composition of zinc oxide 36 per cent, copper oxide 44 per cent, alumina 20 per cent. This mixture was supported on metallic copper in the proportion of 1 of catalyst mixture to 3 of copper: the function of the copper was to minimize local overheating due to the exothermic methanol reaction. These workers prepared the catalyst in a manner similar to that used by Evans and Newton.⁵⁴ The three hydroxides are co-precipitated by ammonia from an aqueous solution of the nitrates at 85° C. With the gel resulting from thorough washing of the precipitate, the metallic copper is incorporated and the mass is then dried at 110° C., giving a granular product. This is placed in the reaction vessel and treated, at 180°–200° C., with the carbon monoxide-hydrogen mixture under a pressure of 6.8 to 26 atmospheres for two to four hours. The copper oxide is, presumably, reduced to copper, the aluminum hydroxide in part dehydrated and, probably, the zinc oxide also in part reduced.⁵⁵

5267A. The close similarity between the decomposition and the synthesis of methyl alcohol previously noted with zinc-copper catalysts is also evident with zinc-chromium oxide catalysts.^{56a} Catalysts containing less than 50 mol per cent of chromium are mixtures of zinc oxide and chromium trioxide, and can be

⁵⁰ Frolich *et al.*, *loc. cit.*

⁵¹ *J. Phys. Chem.*, 1928, **32**, 415.

⁵² *Z. Elektrochem.*, 1928, **34**, 170; *Brit. Chem. Abst.*, 1928, 488A.

⁵³ That is, before reduction.

⁵⁴ *Ind. Eng. Chem.*, 1926, **18**, 513. On catalysts for the production of hydrogen from water-gas.

⁵⁵ See para. 5324, footnote.

^{56a} Cryder and Frolich, *Ind. Eng. Chem.*, 1929, **21**, 867–871; *Brit. Chem. Abst.*, 1929, 934B.

dehydrated and reduced by methyl alcohol at 220°; above 50 per cent the excess chromium is added as the sesquioxide, since then the higher oxide is irregularly

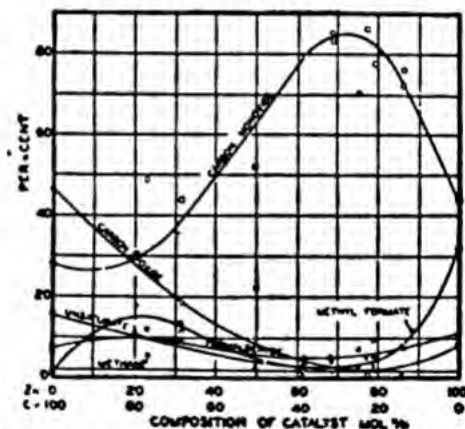


FIG. 141.—PER CENT OF TOTAL DECOMPOSED METHANOL OCCURRING AS CARBON MONOXIDE, CARBON DIOXIDE, METHANE, FORMALDEHYDE, UNSATURATED HYDROCARBONS AND METHYL FORMATE WITH ZINC-CHROMIUM CATALYSTS OF VARIOUS COMPOSITIONS. (Cryder and Frolich.)

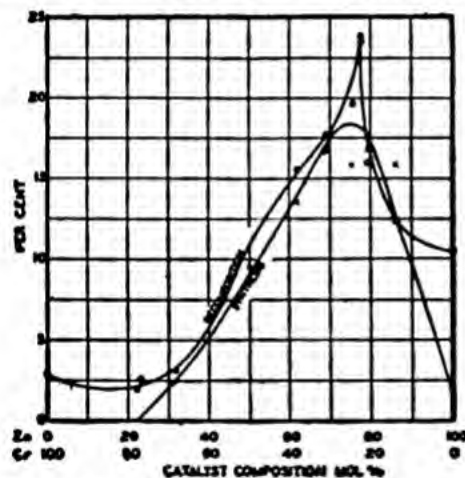


FIG. 142.—TOTAL DECOMPOSITION OF METHANOL AT ATMOSPHERIC PRESSURE AND 340° C., AND SYNTHESIS AT 3000 LBS. PRESSURE (204 ATMOSPHERES), USING A CONSTANT WEIGHT OF THE SAME CATALYST. (Cryder and Frolich.)

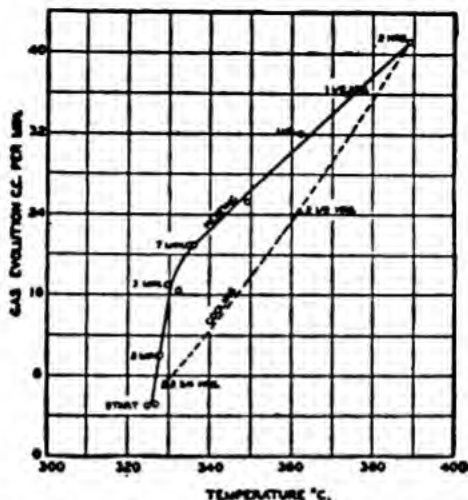


FIG. 143.—EFFECT OF CHANGE OF TEMPERATURE ON ACTIVITY OF A ZINC-CHROMIUM CATALYST FOR DECOMPOSITION OF METHANOL. (Cryder and Frolich.) Catalyst composition: zinc, 75; chromium, 25.

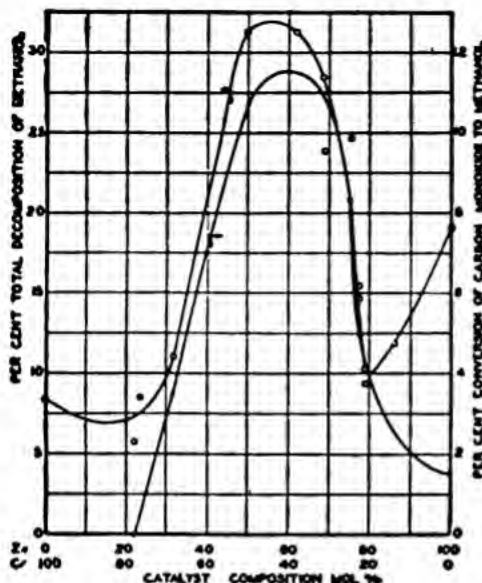


FIG. 144.—TOTAL DECOMPOSITION OF METHANOL AT ATMOSPHERIC PRESSURE AND 340° C., AND SYNTHESIS AT 3000 LBS. PRESSURE (204 ATMOSPHERES), USING AS A BASIS 1 CC. OF SAME CATALYSTS. (Cryder and Frolich.)

reduced. The decomposition experiments, carried out at 1 atmosphere and 340°, show that a maximum yield of carbon monoxide, equivalent to 85 per cent

of the methyl alcohol converted, occurs with a catalyst containing 75 mol per cent zinc. Catalysts richer in chromium give relatively large yields of carbon dioxide and unsaturated hydrocarbons, while those richer in zinc tend to produce methyl formate. The activity of the catalysts, as shown by the amount of alcohol decomposed, has also a sharp maximum at 78 per cent zinc. In the

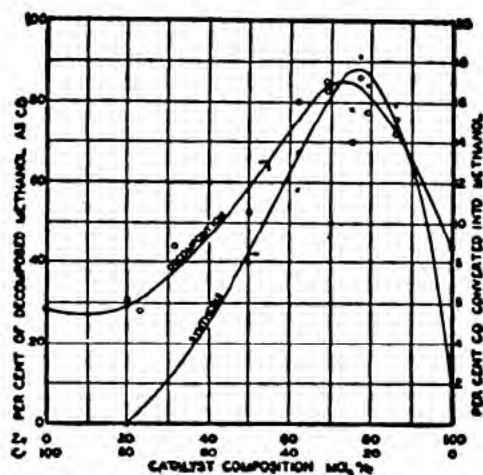


FIG. 145.—COMPARISON OF METHANOL DECOMPOSITION AT 340°C . AND ATMOSPHERIC PRESSURE WITH SYNTHESIS AT 350°C . AND 3000 LBS. (204 ATMOSPHERES) USING SAME CATALYSTS. (Cryder and Frolich.)

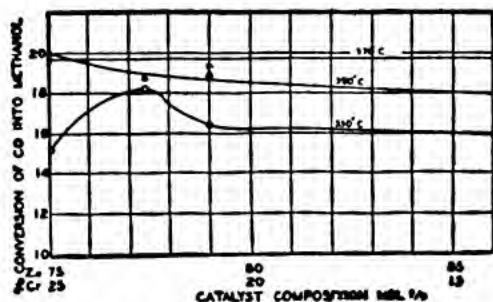


FIG. 146.—EFFECT OF INCREASE IN TEMPERATURE ON YIELD OF METHANOL FROM CARBON MONOXIDE AND HYDROGEN, USING ZINC-CHROMIUM CATALYSTS. (Cryder and Frolich.)

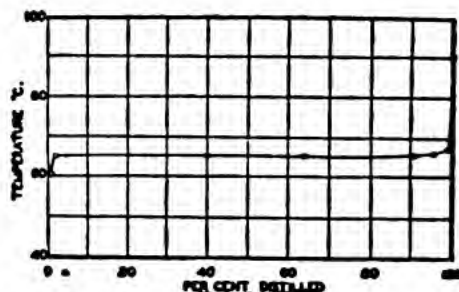


FIG. 147.—DISTILLATION CURVE FOR LIQUID PRODUCT OBTAINED FROM CARBON MONOXIDE AND HYDROGEN AT 3000 LBS. (204 ATMOSPHERES) AND 350°C ., USING ZINC-CHROMIUM CATALYST. (Cryder and Frolich.) Catalyst composition, 4Zn : 1Cr.

synthetic experiments, carried out at 204 atmospheres and 350° , the maximum production of methyl alcohol occurs with a catalyst containing 77 mol per cent zinc, in which case 18 per cent of the carbon monoxide is converted. The optimum temperature for a catalyst of this composition is 370° – 390° ; the liquid product formed is shown by fractionation to be almost pure methyl alcohol. The yield of formaldehyde was almost constant throughout the decomposition

experiments, and it is suggested that this is an intermediate product, which either breaks down to carbon monoxide and hydrogen or yields methyl formate as a condensation product. This work was followed by a study of the properties of a catalyst composed of the oxides of zinc, copper, and chromium, in which the metals are present in the molecular ratio 43 : 49 : 8. The results show that this ternary mixture is far more active in promoting the decomposition and in the synthesis of methyl alcohol than the binary systems copper-zinc and chromium-zinc. The temperature range of the decomposition experiments was 220°–285°. It was found that at temperatures above 250° the alcohol decomposed according to the equation $\text{CH}_3\text{OH} = \text{CO} + 2\text{H}_2$ with very little production of formaldehyde or methyl formate, while at lower temperatures these two substances were found in somewhat larger amount. When methyl alcohol is passed over the catalyst at 180° important quantities of carbon dioxide appear in the exit gas due to the reduction by carbon monoxide of the oxides; the hydrogen also present does not appear to reduce the oxides at temperatures up to 250°. In the synthesis of methanol the conversions are high for this catalyst and it is active at low temperatures.⁵⁴

5268. Chromate Catalysts. Catalysts containing chromium figure largely in the patent literature. Such catalysts were used experimentally by Brown and Galloway and by Morgan, Taylor and Hedley. The latter group used normal zinc chromate, basic zinc chromate, and a mixture of basic zinc chromate and copper; the former group used only the two zinc chromates.

5269. Brown and Galloway prepared normal zinc chromate by mixing zinc oxide to a paste with a small portion of chromic acid solution. This was added to the remainder of the chromic acid solution and the mixture was agitated for twelve to fifteen hours. The precipitated chromate was filtered off, pressed, dried at 80° C. and reduced at 300° C. in hydrogen.

5270. The basic chromate was made by adding zinc nitrate solution (496 g. zinc nitrate, $\text{Zn}(\text{NO}_3)_2$, in 2.4 liters water) to a dilute aqueous solution of 896 g. of sodium chromate, $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$. The precipitate was washed and pressed into threads. These were air-dried, then dried at 80° C. and finally reduced in hydrogen at 300° C.

5271. Morgan and his co-workers prepared their chromate catalysts in a manner substantially the same as that used by Brown and Galloway. They remark that within the limits of 300°–350° C. the temperature of reduction does not seem to affect the activity of catalysts of this type. Data on this point are furnished by the first table on page 650, taken from the article by Brown and Galloway.⁵⁴

5272. It will be seen that the decreasing order of activity is I, III, II, but whether conditions of preparation are alone responsible for the differences is a matter on which Brown and Galloway will not dogmatize. They find the normal chromate more active than the basic salt; it is a robust catalyst.

5273. Other Catalysts. Other catalyst mixtures tested by Morgan, Taylor and Hedley were: zinc dust and zinc oxide, zinc oxide and silver oxide, zinc oxide and uranium oxide, basic zinc chromate with 10 per cent of cadmium carbonate, basic zinc chromate with 5 per cent of copper chromate, and the manganate, molybdate, tungstate, uranate, and vanadate of zinc. The method of testing was to place 6 cc. of the catalyst in the (static) reaction vessel which was heated in the metal bath. This was now quickly filled with carbon monoxide-hydrogen mixture up to 200 atmospheres. The activity of the catalyst was judged by the time taken for a 10 (or in some cases a 20) atmospheres drop in pressure.

⁵⁴ Fenske and Frolich, *Ind. Eng. Chem.*, 1929, **21**, 1052–1055; *Brit. Chem. Abst.*, 1930, 49B.

⁵⁵ *Ind. Eng. Chem.*, 1928, **20**, 964.

RELATION OF METHOD OF REDUCTION TO ACTIVITY OF CATALYST

Catalyst: Reduced Basic Zinc Chromate. Conditions of Test, 180 Atmospheres, 400° C.

Catalyst	Volume, Cubic Centi- meters	Weight, Grams	Zinc Oxide Content, Grams	Methanol Yield, Grams per Hour		Conditions of Reduction
				Space Velocity 16,000	Space Velocity 7,500	
I	250	165	112.5	129.3	At 40 atmospheres of CO : H ₂ , 1 : 2 mixture; temperature raised slowly from 25° to 370° C.
II	250	153	104.0	89.2	60.8	H ₂ , 1 atmosphere; reduction ini- tiated at 300° C. but tempera- ture uncontrolled, allowed to rise above 450° C.
III	250	170	115.5	106.4	94.5	Reduced at 275°-325° C. at 1 atmosphere with a mixture of 5 per cent H ₂ , and 95 per cent CO.

The following table, taken from the article by Morgan, Taylor and Hedley,⁵⁷ gives a series of average results:

Catalyst	Time in Minutes Taken for 10 Atmospheres Drop in Pressure						
	290°	310°	330°	350°	370°	390°	410°
Zinc oxide	10.0	3.5	3.1
Zinc basic chromate	4.5	1.0	0.8	1.2
Zinc chromate	1.3	0.7	0.6	0.5	0.5
Zinc basic chromate and copper	6.0	1.5	0.8	0.6	0.6	0.9
Zinc manganate	5.2	1.6
Zinc oxide and zinc dust	7.0	1.5
Basic zinc chromate and copper	Time in Minutes Taken for 20 Atmospheres Drop in Pressure						
	14.5	4.5	2.8	2.2	3.5	5.8

5274. From these preliminary experiments it was possible to forecast that: (1) The catalyst prepared from basic zinc chromate or normal zinc chromate would probably prove an efficient catalyst for methyl alcohol syntheses. (2) The temperature of the catalyst should lie between 350° and 400°. (3) A pressure of the order of 200 atmospheres should give a reasonable output of methyl alcohol. With a catalyst prepared either from normal zinc chromate, or from the basic salt, 3ZnO·CrO₃, working at 420° under a pressure of 200 atmospheres at a rate per hour of 2000 liters of gas (N.T.P.) through 60 cc. of catalyst, the hourly output of organic products was about twice the catalyst volume. The liquid

⁵⁷ J.S.C.I., 1928, 47, 122T.

obtained was homogeneous: it contained 95 per cent of methyl alcohol, 1 per cent of higher alcohols and 4 per cent of water. The addition of alkaline substances to the zinc chromate catalyst favored the formation of higher alcohols. Then, to the methanol catalyst (zinc chromate) varying proportions of cobalt chromate were added, with the result that, although methyl alcohol remained the predominant constituent, higher alcohols, including ethyl alcohol, were produced in appreciable quantities, together with small amounts of aldehydes. By the use of mixed cobalt catalysts also, containing copper, zinc, chromium or manganese, alcohols in addition to methyl and ethyl alcohols were identified, namely, *n*-propyl, *n*-butyl, and isobutyl. The alcohols detected were primary. Aldehydic products also were identified; namely, formaldehyde, acetaldehyde, propaldehyde and *n*-butaldehyde. There was indirect evidence of the presence of aldehydals, $R \cdot CH(OX)_2$, the ortho-ethers of the aldehydes.^{57a}

5275. Taylor and Kistiakowsky⁵⁸ find the adsorption of hydrogen and of the oxides of carbon on clean surfaces of the zinc oxide and especially of the zinc oxide with chromium oxide catalysts is many times greater than that on the surfaces of metal hydrogenation catalysts. Moreover, saturation occurs at very low pressure which argues a considerable active surface per unit weight of material.

5276. An important study of the methanol synthesis by Audibert and Raigneau⁵⁹ deals with various catalysts. While the most active single catalysts were found to be copper (metal) and zinc oxide, both were very sensitive to heat. Mixed catalysts were more active and more resistant to heat. While the results with mixed catalysts were somewhat capricious, it seems that the best all-round catalyst was a mixture of reduced copper 100, manganous oxide 37.5, with the addition of chromium sesquioxide in quantity up to 1 atom chromium to 10 atoms copper.

5277. Storch studied the behavior of zinc oxide and zinc oxide-chromium oxide catalysts in the decomposition and synthesis of methanol.⁶⁰ Comparison of various catalysts working with $4H_2 : 1 CO$ gas mixture at 200 atmospheres and 350° C. gave as a result that the catalyst with a composition 11 g. chromic oxide to 100 g. zinc oxide was more active than either oxide alone. Below 300° this catalyst was almost inactive for the methanol synthesis, and at 350° C. the yield was less than at 330° C. No difference was found between the mixed and the single catalysts in the decomposition of methanol at atmospheric pressure.

5278. Frolich, Davidson and Fenske made X-ray examinations of methanol catalysts composed of copper and zinc.⁶¹ The results point to a definite relation between the specific catalytic effect and the distance between the atoms of the two components. Zinc oxide is partly reduced in the presence of copper oxide.⁶²

^{57a} *Chem. Age* (London), 1930, 288.

⁵⁸ *J. Am. Chem. Soc.*, 1927, 49, 2468.

⁵⁹ *Ind. Eng. Chem.*, 1928, 20, 1105: the work on copper catalysts has already been summarized in paras. 5263-5265.

⁶⁰ *J. Phys. Chem.*, 1928, 32, 1743.

⁶¹ *Ind. Eng. Chem.*, Feb. 1, 1928, 109.

⁶² *Chem. Age* (London), 1929, 20, 187. Cf. Frolich. The rôle of catalysts in the high-pressure syntheses from water-gas. *J.S.C.I.*, 1928, 47, 173T.

CHAPTER LIII

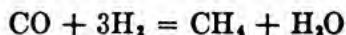
REDUCTION OF CARBON OXIDES

I. METHANOL SYNTHESIS

5300. Until 1923 the sole commercial source of methanol (methyl alcohol) was crude "wood spirit," produced by the destructive distillation of wood: Hence one of its names is wood alcohol. In that year consternation was produced in the wood distillation industry by the announcement that a commercially practicable and cheap synthesis of methanol was in actual operation in Europe. This process was said to produce a high grade of methanol that could be sold at 20-30 cents a gallon. In fact this product was imported and sold at a price (45 cents a gallon) with which the wood distillers could not compete.¹ Somehow or other, this competition seems to have been eliminated and the price of impure methyl alcohol of denaturing quality, at the time of writing, more nearly corresponds to the average price of former days. One of the factors that has greatly assisted the old established domestic industry is that the Government specifies the product of wood distillation for denaturing alcohol.

5301. Notwithstanding that, for the present, the menace to the wood distillation industry of fatal competition from the synthetic product has been sidestepped, the process for synthesizing methanol is a practical success.

5302. Several methods that have been published start with water-gas as the raw material. Water-gas is the product of the action of steam on coke: ideally it should consist of equal volumes of carbon monoxide and hydrogen. If such a mixture is passed over a nickel catalyst at atmospheric pressure and at a temperature of 380° C. the product is a mixture of carbon dioxide (52.6 per cent), methane (39.8 per cent) and hydrogen (7 per cent).² If the mixture is enriched so that the hydrogen is in the proportion of 1 volume to 1 of carbon monoxide, the conversion to methane is almost complete at 230°-250° C. This reaction (as completed) may be written:



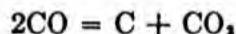
while the first reaction is in the direction of:



¹ *Paint, Oil and Chemical Review*, Oct. 14, 1926. The President of the United States on November 27, 1926, increased the import duty on methyl or wood alcohol (or methanol) from 12 to 18 cents per gallon under the provisions of Section 315 of the Tariff Act (i.e., the "flexible tariff" provisions). *Chem. Age* (London), 1927, **16**, 77.

² Sabatier, *Catalysis*, 394.

At the higher temperatures the operations are complicated by the reaction:



with the deposit of carbon and subsequent partial hydrogenation of the carbon dioxide.

5303. With the use of high pressures and temperatures, suitable catalysts and special precautions, methanol is the chief product. This is the fundamental principle of the various processes that have been published. The information available is found chiefly in the patent literature: so far as one can judge the methods seem to differ from one another mainly in the catalysts used.^{2a}

5304. One striking peculiarity of the method is the necessity for excluding iron, and also nickel and cobalt. These metals catalyze other reactions and especially the complete hydrogenation to methane. So important is this that in addition to the usual purification from sulphur, etc., the gases undergo treatment to remove traces of carbonyls. According to one patent³ this is effected by passing the mixture of oxides of carbon and hydrogen through activated carbon. Evidently no iron or nickel can be used in parts of the apparatus exposed to the gases: the apparatus must be lined with copper.

5305. Some of the specifications also rule out the alkalis. The reason for this is, as we shall see when we come to discuss synthetic fuels, that alkalis promote the formation of complex mixtures consisting, in large part, of the higher homologs of methanol.

5306. Composition of Reactant Gases. The typical composition of the gas mixture for the methanol synthesis is: carbon monoxide and hydrogen, the latter in greater volume, with or without an admixture of carbon dioxide, hydrocarbons and inert gases, carefully purified, especially from volatile iron compounds and iron particles.

Example. Hydrogen 80 per cent, carbon monoxide 20 per cent, both by volume. Inert gases may be present.⁴

5306A. Sometimes the wording indicates that carbon dioxide may be substituted entirely for the monoxide and no mention is made of any modification of the conditions that this may necessitate.

Example. "... the reduction of carbon monoxid or carbon dioxid . . . "
"... a mixture of carbon oxids with at least about an equal volume of hydrogen . . . "

5307. According to Dreyfus⁵ an excess of hydrogen is not necessary. The proportion ordinarily found in water-gas may be used in the synthetic production of methanol, if zinc oxide alone is used as the catalyst. The ratio may be 1 molecule of hydrogen, or less, to 1 molecule of carbon monoxide. The temperature is preferably 200° to 300° C., the pressure 50 to 150 atmospheres.

^{2a} On the simultaneous formation of dimethyl ether see Brown and Galloway, *Ind. Eng. Chem.*, 1929, **21**, 310; *Brit. Chem. Abst.*, 1929, 426B.

³ Canadian Pat. 251,485, July 7, 1925, to Pier, Müller, Wietzel and Winkler.

⁴ U. S. Pat. 1,569,775, 1926, to Mittasch, a Badische Co. patent.

⁵ U. S. Pat. 1,558,559, to Mittasch, a Badische Co. patent.

⁶ Brit. Pat. 262,494, 1925; *Chem. Age* (London), 1927, **46**, 69. See para. 5310.

5308. A gas mixture obtained by distilling bituminous coal or by a cracking process has been employed in methanol synthesis. The hydrocarbons in these gases are partly oxidized with a restricted quantity of oxygen to convert part or all of them into carbon monoxide and hydrogen. The sulphur compounds are removed and the mixture then passes over a catalyst to produce methanol.⁷ Another suggestion is that mixtures of water-gas and gases partially or wholly burnt or gases of like composition and containing hydrocarbons previously transformed into carbon monoxide, carbon dioxide, water and hydrogen be used for the production of methanol and ammonia.^{7a} It has also been proposed that gases containing gaseous paraffin hydrocarbons such as natural gases, gases from cracking plants, stills or low-temperature carbonisation retorts be passed through a preheater at a temperature below that at which decomposition occurs (below 550°) and then through reaction tubes or passages heated to definite temperatures for different gases (ranging from 650–750° for pentane to 850–975° for methane) with or without addition of superheated steam.^{7b}

5309. In the catalytic production of methanol or other oxygenated organic compounds from carbon oxides and hydrogen at high temperatures and pressures, gas mixtures are employed containing a high percentage of gases not required for the reaction. Part of the circulating gases rich in inert gas is continuously removed and replaced by fresh gas mixture in such proportion as to maintain a constant composition of the circulating gas. By using inert gases, the excess heat developed is absorbed and the yield obtained is equal to or higher than that obtained with pure gases. It is possible to use gases which are available in large quantities at a low cost, and an example is given of the use of a gas containing 5.5 per cent carbon dioxide, 27.8 per cent carbon monoxide, 15.6 per cent hydrogen, 2.6 per cent methane, and 48.5 per cent nitrogen. The gas is mixed with steam and passed over heated iron oxide to decompose so much of the carbon monoxide that the gas contains carbon monoxide and hydrogen in the proportion of 1 : 2. The carbon dioxide is absorbed by water, and the gas then circulated over a contact mass at a pressure of 1000 atmospheres and a temperature of 400° C. When the proportion of reacting constituents has decreased from 45.9 per cent to 36 per cent, this proportion is maintained by continuous withdrawal of circulating gas and addition of fresh gas.⁸ Another proposal is to introduce a gas such as nitrogen or an excess of hydrogen into the gas mixture before reaction, and with a mixture of suitable composition the production of ammonia may be combined with that of oxygenated organic compounds.^{8a}

5310. Dreyfus describes the making of methanol by passage of an equimolecular mixture of hydrogen and carbon monoxide over a plain zinc oxide catalyst at a temperature of 200°–450° C., and under a pressure normally from 50–150 atmospheres and upwards to 200 atmospheres. A copper-lined or aluminum apparatus is preferred. If the gases are passed at a low speed, higher alcohols with hydrocarbons are formed.⁹

5311. Conditions of Operation. Kelley¹⁰ arrives, by purely thermodynamic reasoning, at the conclusion that the methanol synthesis is workable up to a temperature of 700° A. (427° C.). Patart's¹¹ experimental results give an optimum temperature between 600° and 900° A. (327° to 627° C.) at 150 atmospheres.

⁷ Brit. Pat. 266,410, Oct. 23, 1925, to Johnson, a Badische Co. communication; *Chem. Age* (London), 1927, 16, 338.

^{7a} Soc. Chim. de la Grande Paroisse (Azote et Produits Chimiques), French Pat. 35,096, Feb. 22, 1928; Addn. to 649,711; *Chem. Abst.*, 1930, 1942.

^{7b} Anglo-Persian Oil Co., Ltd., Dunstan and Wheeler, Brit. Pat. 309,455, Oct. 8, 1928; *Chem. Abst.*, 1930, 719.

⁸ Brit. Pat. 266,405, Oct. 19, 1925, to Johnson, a Badische Co. communication; *Chem. Age* (London), 1927, 16, 338.

^{8a} Soc. L'Air Liquide, Soc. Anon. pour L'Etude et L'Exploitation des Procédés G. Claude, Brit. Pat. 306,512, Feb. 22, 1928; *Chem. Abst.*, 1929, 4949.

⁹ *Chem. Abst.*, 1927, 21, 3626; Brit. Pat. 262,494, June 13, 1925. See also U. S. Pat. 1,738,989, Dec. 10, 1929, to Dreyfus.

¹⁰ *Loc. cit.*

¹¹ Lormand, *Ind. Eng. Chem.*, 1925, 17, 430.

5312. The conditions specified by Mittasch are: "... pressure being preferably from 50 atmospheres upwards and the temperature between say about 250° and 600° C., depending on the efficiency of the contact mass in each individual case." In the example given the pressure is said to be about 220 atmospheres and the temperature 450° C.¹²

5313. **Equilibrium Constants of the Methanol Synthesis.** Kelley¹³ calculated the methanol equilibrium constant, and gave the following as the equation of the free energy change of the reactions:

$$\Delta F = -21,300 + 32.2T \log T - 0.00825T^2 - 42.5T.$$

The equilibrium constant is

$$\log_e K_p = \Delta F/(-RT)$$

5314. These results have been criticized.¹⁴ Kelley has derived the free energy of the reaction at 298° A., from data which do not involve the specific heat of methyl alcohol in the gaseous phase, and it is probable that incorrect assumptions have been made for this temperature effect in the calculations of the free energy change at the higher temperatures.

5315. Audibert and Raineau have produced the following equations for the methyl alcohol equilibrium starting with a gaseous mixture of the composition (CO + 2H₂). The fraction x of carbon monoxide converted into methyl alcohol is approximately given by Nernst's method of evaluation.

$$\log [(1-x)^2/x(3-2x)^2] = -27,000/(4.571T) + 3.5 \log T + 2.99794 - 2 \log P$$

This relationship may be expressed on the basis of partial pressures as follows:

$$\log K_p = P_{\text{MeOH}}/P_{\text{CO}}[P_{\text{H}_2}]^2 = 27,000/(4.571T) - 3.5 \log T - 3.6$$

From the preceding expression it appears that Audibert and Raineau, by taking the algebraic sum of the chemical constants as 3.6, have deduced an equation for the equilibrium constant in close agreement with experimental results.¹⁵

¹² Mittasch, U. S. Pat. 1,558,559. The same as in 1,569,775.

¹³ *Ind. Eng. Chem.*, 1926, **18**, 78. A thermodynamic consideration of the methanol process.

¹⁴ Morgan, Taylor and Hedley, *loc. cit.*; Francis, *Ind. Eng. Chem.*, 1928, **19**, 284; "Calculations of the methanol equilibrium are bound to be more or less inaccurate owing to the lack of adequate data on the specific heat and the equation of state of the alcohol." Lewis and Frolich, *Ind. Eng. Chem.*, 1928, **20**, 287. Kelley himself has recently recalculated these values, using new data. He obtained the following values, which he offers without much confidence:

$$\Delta F^\circ_{298} = -9640 \text{ cal. and } \Delta H_{298} = -25,150 \text{ cal.}$$

$$\Delta F^\circ = -20,740 + 4500T \log_{10} T - 0.01586T^2 + IT$$

$$\text{where } I = 69.4.$$

The discrepancy between calculated and directly measured values of K_p is ascribed by Dodge to an inaccuracy in the value of the heat of combustion of methanol. If we are to calculate, even roughly, equilibria for reactions of this type, we must have very accurate heat-of-reaction data. As a further concrete illustration of this fact it may be readily calculated that, if the value for the heat of combustion of methanol were in error by only 0.10 per cent, the K_p for the reaction at 298.1° K. would be in error by approximately 33 per cent as a result. In other words, a calculation of the free-energy change for the methanol-synthesis reaction, though based on the third law, and therefore requiring a knowledge of absolute entropies is nevertheless far more dependent on exact data for the various heats of reaction than on the entropy data. [*Ind. Eng. Chem.*, 1930, **22**, 89.]

¹⁵ Morgan, Taylor and Hedley, *loc. cit.*

5316A. Further experimentation at Teddington on the methanol equilibrium under various conditions of temperature and pressure has given results in close agreement with Audibert's formula.

5316. Francis (*loc. cit.*) gives the following equation and values derived from it for the methanol synthesis:

$$\Delta F = -26,370 + 49.9 T$$

Applying this we have:

°C.	ΔF
227°	- 1420
327°	+ 3570
427°	+ 8560

METHANOL EQUILIBRIUM CONSTANT

Temperature		Equilibrium Constant $K = \frac{\text{CH}_3\text{OH}}{(\text{CO})(\text{H}_2)^2}$ According to:		
Absolute	Degrees C.	Audibert	Kelley	Francis
300°	27°	2.65×10^7	6.70×10^7	
400°	127°	1.15×10^3	20.6×10^3	
500°	227°	5.75×10^{-2}	316.0×10^{-2}	417×10^{-2}
600°	327°	3.20×10^{-4}	386.0×10^{-4}	500×10^{-4}
700°	427°	7.55×10^{-6}	1540.0×10^{-6}	2100×10^{-6}

5317. The figures given by the equations of Francis and of Kelley are of the same order of magnitude, but between them and those derived from Audibert's equation there is a discrepancy which widens as the temperature rises.

5318. Further experimentation, according to Morgan, Taylor and Hedley (*loc. cit.*) has confirmed the applicability of Audibert's formula in the conditions of practice.

5319. Equilibrium Conditions in the Formation of Hydrocarbons and Alcohols from Water-gas.¹⁶ Conclusions: (1) It is easier to form higher than it is to form lower paraffins at all temperatures. Given suitable catalysts it should be possible to form any of the paraffins at atmospheric pressure and at 300° C. Increase of pressure tends to increase of molecular weight of the product.

(2) The tendency to form cyclic hydrocarbons and especially benzene is in general greater than the tendency to form straight chain hydrocarbons.

(3) The lower alcohols cannot and the higher alcohols can be formed at atmospheric pressure and 300° C.

(4) The tendency to all these syntheses falls off rather rapidly with increase of pressure.

(5) Tables are given from which may be computed the maximum possible yields.¹⁷

5320. Fieldner and Brown¹⁸ have compared the experimental values they obtained with those given by other workers (Audibert and Raineau, Lewis and Frolich). Using a development of the Nernst approximation formula, K_p has been calculated from the results of different workers, assuming no departure from the perfect gas laws. The values of K_p obtained are of the same order and vary as might be expected from the activities of the catalyst employed and the relative space velocities used. Taking into account deviations from the perfect gas laws, the fugacities (effective pressures) and the partial fugacities of the components have been calculated from the results of the three sets of investigators.

¹⁶ Smith, *Ind. & Eng. Chem.*, 1927, **19**, 801.

¹⁷ For the polemic to which this paper gave rise see: Tropsch, *Brennstoff-Chem.*, Dec. 1, 1927, 376; Smith's reply, *ibid.*, 1928, 248; further comment by Tropsch, *ibid.*, 250.

¹⁸ *Ind. Eng. Chem.*, 1928, **20**, 1110.

From the partial fugacities a new set of K values, designated K_f , is calculated; the values, as for K_p , are of the same magnitude. Space-time yields are also discussed.¹⁹

5321. A preliminary paper on the equilibrium between methanol, carbon monoxide and hydrogen has been published by Smith and Branting of the Pittsburgh Station of the U. S. Bureau of Mines.²⁰ They compare their preliminary results with those published by others, either on experimental or theoretical grounds. There is a wide divergence from Kelley's calculations that still remains to be cleared up. See paragraph 5321B. Experimental yields approximate as closely as may be expected from conditions not strictly arranged to produce equilibrium.

5321A. The equilibrium constant:

$$K = \frac{\text{CH}_3\text{OH}}{(\text{CO})(\text{H}_2)^2}$$

is 5.57×10^{-4} at 303.8° C., with a probable error of ± 5 per cent.

The equation for the standard free-energy change in the methanol reaction, derived from these equilibrium measurements and from the best available heat data is:

$$\Delta F = -20,857 + 41.17T \log T - 0.1423T^2 - 54.42T.$$

5321B. Newitt, Byrne and Strong,^{20a} by an experimental method, arrive at the following expression for the free energy:

$$\Delta F = 70.5T - 30,500.$$

Bone refers to the work of Newitt, Byrne and Strong,^{20a} observing that at high pressures equilibrium determinations can be considered satisfactory only when approaches are made to the equilibrium from *both* sides. In order to ensure accuracy in the determinations of K_p it was decided to employ two independent experimental methods, namely, a "static" and a "flow" method, respectively, and in each case to approach the equilibrium from both sides, i.e., from both the synthesis and decomposition of methyl alcohol. Using a suitably reduced $3\text{ZnO} \cdot \text{Cr}_2\text{O}_3$ catalyst to which 0.5 per cent copper nitrate had been added, a temperature range from 280° to 338° C., and pressures between 60 and 100 atmospheres—conditions under which a mixture of one volume of carbonic oxide and two volumes of hydrogen was found to produce methyl alcohol to the practical exclusion of other products—and at each experimental temperature approaching the equilibrium from *both* sides by each of the two methods referred to, practically identical results for the equilibrium conditions at each temperature were obtained. Two examples may be given. By the "static" method the value of K_p at 320° C. was found to be 6.7×10^{-5} when equilibrium was approached from the excess methyl alcohol side, and 6.4×10^{-5} when approached from the other side; at 338° C. the two experimental values were 4.3×10^{-5} and 4.6×10^{-5} , respectively—and by interpolation the value at 330° C. would be 5.5×10^{-5} . By the "flow" method the experimental value at 330° C. was 5.2×10^{-5} . The results as a whole showed the following linear relationship between the free energy and absolute temperature: $\Delta F = 70.5T - 30,500$. The following K_p values were calculated for every 20° C. over the range 260° to 380°, which is the most practicable for the synthesis of a substantially pure methyl alcohol from a $\text{CO} + 2\text{H}_2$ mixture:

Temperature	K_p	Temperature	K_p
° C.		° C.	
260	1.2×10^{-5}	340	2.9×10^{-5}
280	4.5×10^{-5}	360	1.3×10^{-5}
300	1.6×10^{-4}	380	6.3×10^{-6}
320	6.7×10^{-5}		

¹⁹ *Brit. Chem. Abst.*, **1928**, 920B.

²⁰ *J. Am. Chem. Soc.*, 1929, **51**, 129.

^{20a} *Proc. Roy. Soc.*, 1929, **A123**, 236; *Chem. Abst.*, 1929, **23**, 3148; *Brit. Chem. Abst.*, **1929**, 508A.

^{20b} Discussion on Catalytic Reactions at High Pressures, *Proc. Royal Soc.*, **1930**, A127.

These values are stated by Bone to be considerably lower than any corresponding values either calculated or experimentally obtained by previous workers. Thus, for example, taking 200 atmospheres as a practical working pressure and 600° K. (327° C.) as temperature, according to the determinations of Newitt and his collaborators the partial pressure of the three components of the equilibrium mixture $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ would be:

$$\text{CO} = 54.5, \quad \text{H}_2 = 109.0, \quad \text{and} \quad \text{CH}_3\text{OH} = 36.5 \text{ atmospheres.}$$

Whereas, from Audibert and Raineau's calculated K_p for 600° K. and 200 atmospheres pressure, we should expect

$$\text{CO} = 39.0, \quad \text{H}_2 = 78.0, \quad \text{and} \quad \text{CH}_3\text{OH} = 83.0 \text{ atmospheres,}$$

and from Kelley's calculated K_p ,

$$\text{CO} = 10.4, \quad \text{H}_2 = 20.8, \quad \text{and} \quad \text{CH}_3\text{OH} = 168.2 \text{ atmospheres.}$$

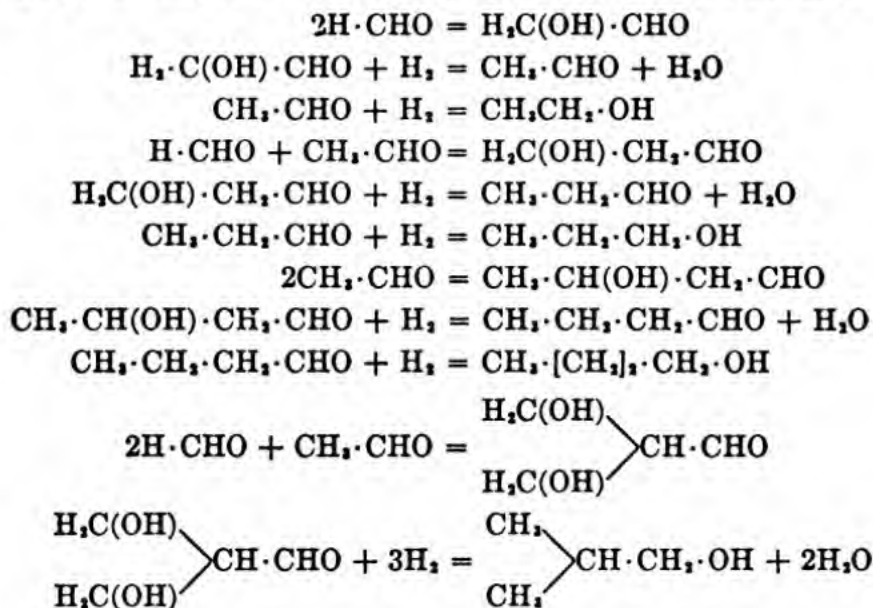
Bone observes that the correct determination of K_p values in such a system is of considerable commercial as well as scientific interest, inasmuch as such values are the best criteria of the efficiency of a catalyst at a given temperature. For example, if by using a given catalyst at a given temperature a quantitative yield of methyl alcohol near to that of the equilibrium proportions predicted by the experimental K_p values at such temperature were readily secured the quest for a more active catalyst would be unnecessary.

5321C. Hypotheses Concerning the Mechanism of Methanol Syntheses. As may be expected, there is some divergence of opinion regarding the course of the several reactions which would serve to explain the formation of methanol and other compounds (of higher molecular weight) from carbon monoxide (or dioxide) and hydrogen. Morgan²⁰ advocates a series of reactions which are given below. He refers to the work of Fischer and Tropsch with alkalized iron which led these investigators to suggest that the oxygenated products were formed by the synthesis of methyl alcohol followed by the direct addition of carbon monoxide to this alcohol, with production of acetic acid from which acetone is formed by loss of carbon dioxide. This scheme accounts for the presence of acids, ketones and higher alcohols. Zinc formate on heating decomposes into zinc carbonate, formaldehyde, methyl formate and methyl alcohol. Under the conditions of the methanol synthesis, zinc formate might play the part of an unstable intermediate compound which is continually being regenerated and decomposed.



²⁰ "Discussion on Catalytic Reactions at High Pressures" opened by G. T. Morgan, *Proc. Royal Soc.* 1930, A, Vol. 127.

Higher Aldehydes and Alcohols by repeated Aldolization and Hydrogenation.



This sequence continues to yield still higher alcohols. The aldolization hypothesis accounts for the products hitherto isolated, but it also postulates the transitory existence of intermediate hydroxyaldehydes and glycols which have not so far been detected. These substances may, however, be transformed by dehydration into unsaturated aldehydes and alcohols which would speedily undergo hydrogenation to saturated aldehydes and alcohols. If substantiated by further experiment, this aldolization hypothesis brings the syntheses of homologous alcohols by high-pressure catalysis into line with the transformations following on photosynthesis which take place through the agency of living organisms (bacteria, yeasts, moulds and the green plant). With more efficacious catalysts and less elevated temperatures one may anticipate that this analogy will become increasingly closer.²⁰

5322. Composition of Catalysts. The catalysts used fall into three classes:

- (1) Mixtures of metallic oxides. (2) Mixtures of metals (including alloys).
- (3) Mixtures of oxides and metals, or a metal plus an oxide or salt as promoter.

5323. Mixtures of Metallic Oxides. The most general statement is a mixture of oxides of different groups in the periodic system, not reducible to metal in the conditions prevailing. This becomes more specific in the form: "Nonreducible oxides of the second to the seventh group of the periodic system are especially suited for such mixed catalysts."²¹ The same patent specifies that the more basic oxide should be in considerable excess and instances: zinc oxide and chromium oxide (2 to 12 mol. wts. of zinc oxide to 1 mol. wt. of chromium oxide); oxides of—zinc and uranium, zinc and vanadium, zinc and tungsten, magnesium and molybdenum, cerium and manganese. See paragraph 5324.

5323A. Patart (who is generally credited with being the earliest successful worker in this line) specifies a mixture of 90 parts of copper oxide to 10 parts of zinc oxide.²² Under working conditions the copper oxide would, seemingly, be reduced.

²⁰ Morgan, *ibid.*

²¹ U. S. Pat. 1,558,559, 1925, to Mittasch.

²² Cf. Lormand, *Chem. Abst.*, 1925, 19, 2027.

5323B. Audibert²² uses catalysts said to consist of the *suboxides* of vanadium, manganese, tungsten, lead and bismuth.

5324. *Mixtures of Metals with Oxides or Salts.* We have already indicated that Patart's catalyst, described as a mixture of copper oxide and zinc oxide may, in use, become a mixture of metallic copper and zinc oxide.²⁴ Mixed catalysts containing metal and oxide or salt are mentioned by Mittasch²⁵ as follows: "... metals such as copper, silver, lead, zinc in conjunction with a metal oxide or a metal salt acting as promoter especially derived from a metal belonging to the fourth to the seventh groups of the periodic system." See paragraph 5323.

5324A. Mittasch also mentions that by the use of irreducible oxide catalysts with a small addition of potassium carbonate, a higher percentage of carbon monoxide and a reduced velocity of the gas current, higher alcohols such as propyl, butyl and amyl alcohols are formed, as well as methanol, the proportions varying with the conditions.

5325. Grenier²⁶ uses wood charcoal as a catalyst in the production of hydrogen from carbon monoxide and steam or in the synthesis of methanol from carbon monoxide and hydrogen.²⁷

5326. *Copper Catalyst for Methanol Synthesis.* Audibert prepares a catalyst by treating a solution of copper nitrate or of a copper organic salt with alkali, washing the precipitate, drying it *in vacuo*, mixing with a small amount of violet-colored copper and reducing at a temperature not exceeding 200° C. with hydrogen or carbon monoxide, at ordinary pressure, with or without a diluent such as nitrogen or methane. Over this is passed water-gas preheated (not over 180° C.) under a pressure of 100 atmospheres and at a temperature not exceeding 450° C. at any point.²⁸

5327. Three U. S. patents to Storch²⁹ disclose a method of producing copper-containing catalysts by adding sodium hydroxide to a solution of a cuprammonium compound, boiling to expel ammonia, and reducing the washed and dried precipitate in hydrogen. 1,681,750 describes a catalyst composed of copper, prepared in this way, which may be supported on an inert carrier. 1,681,752 deals with catalysts containing, in addition to the copper, a fluoride of an alkaline earth metal. 1,681,753 claims a mixture of copper obtained as described, with magnesium oxide. The method of preparation is given in detail.

5327A. Another catalyst for the synthesis of methanol from carbon monoxide and hydrogen proposed by Storch^{29a} contains copper, magnesia and silica. It is prepared by reacting on magnesium nitrate and copper nitrate with sodium silicate and sodium hydroxide. The precipitate which forms is filtered and washed, dried and preferably pressed into tablets and reduced. Storch has used hydrogen saturated with methanol as a reducing agent. The reducing gas is usually diluted with nitrogen in order better to control the temperature during reduction. Storch recommends a mixture of three volumes hydrogen, two volumes methanol vapor and 95 volumes nitrogen, conducting the reduction normally at 150–200° C. A gas mixture of four volumes hydrogen and one volume carbon monoxide then is passed through the catalyst at 270° C. and 200 atmospheres pressure.

5328. *Copper Catalyst.* A boiling solution of copper sulphate or nitrate, free from impurities (especially iron), is treated with caustic alkali, and the black hydrated oxide, washed free from alkali and dried in a vacuum at 50°, is mixed with 10–20 per cent of the violet modification of metallic copper (Sabatier) and reduced at the ordinary pressure by hydrogen or carbon monoxide in a slow stream or diluted with nitrogen or methane not above 130°–140°. The resulting porous, fine-grained, pyrophoric catalyst converts hydrogen and carbon monoxide at 275°–300° and 100–200 atmospheres into methyl alcohol and formaldehyde.³⁰

²² *Chem. Abst.*, 1925, 2403.

²⁴ With some metallic zinc. Brit. Pat. 237,030 confirmed by Rogers, *J. Am. Chem. Soc.*, 1927, **49**, 1432.

²⁵ U. S. Pat. 1,569,775, 1926.

²⁶ Brit. Pat. application 271,523, convention date May 22, 1926; *Chem. Age* (London), 1927, **17**, 115.

²⁷ Compardou and Vergues, French Pat. 613,470, Mar. 3, 1925, also specify wood charcoal as a methanol catalyst.

²⁸ Brit. Pat. 271,538, Jan. 30, 1926; *Chem. Abst.*, 1928, **22**, 1596.

²⁹ U. S. Pats. 1,681,750, 1,681,751, 1,681,752, Aug. 21, 1928.

^{29a} U. S. Pat. 1,738,971, Dec. 10, 1929, assigned to Roessler & Hasslacher Chemical Company.

³⁰ French Pat. 606,596, Feb. 27, 1925, to Soc. nat. de recherches sur le traitement des combustibles; *Brit. Chem. Abst.*, 1928, 857B.

5329. A simpler method³¹ is described below. Carbon monoxide and hydrogen are passed at 160°–180° and 150 atmospheres pressure over a catalyst consisting of precipitated copper hydroxide reduced in hydrogen at ordinary pressure; reduction begins at 140°, and the temperature must not exceed 450°–500°.³²

5330. Copper with Zinc Oxide³³ as a methanol catalyst is prepared as follows: Copper oxide 4, zinc oxide 96 in intimate mixture are prepared by co-precipitation from mixed solutions by boiling alkali; the dried precipitate is reduced with hydrogen or carbon monoxide at the lowest possible temperature.

5331. Catalysts from Carbonyls.³⁴ Catalysts are prepared for the carbon oxides syntheses by thermal decomposition of the carbonyls of iron, cobalt, nickel and molybdenum.³⁵

5332. In another British patent, 270,705, May 10, 1926, to the I. G., the addition of ammonia is claimed to facilitate the process. The liberated metal, collected in dust chambers, may be treated with activated silica to adsorb hydrocarbons. *Chem. Abst.*, 1928, **23**, 1672.

5333. Hydrogen in excess, mixed with carbon monoxide or dioxide, is subjected to a pressure of not less than 30 atmospheres at 200° C. in presence of a catalyst. The catalyst contains copper and one of the elements titanium, vanadium, chromium, manganese, boron, but must be free from iron and nickel.³⁶

5334. Gabriel and Brown³⁷ obtain methanol by passing a 1 : 5 mixture of carbon monoxide and hydrogen over a copper-zinc alloy, containing some unreduced oxides, at 280° C. under a pressure of 20 atmospheres.

5335. Catalysts for carbon oxide reductions³⁸ containing nickel with irreducible oxides are described by the Compagnie de Béthune. For example, activated charcoal is heated and immersed in a solution of zinc and chromium formates containing a small quantity of nickel formate: the mass is dried.

5336. The same company makes catalysts for the methanol synthesis by depositing formates of uranium, tungsten, vanadium, zinc, beryllium, chromium or titanium on a porous support.³⁹

5337. Two mixed catalysts, metallic strontium with litharge, and metallic zinc with bismuth oxide for the methanol synthesis, are proposed by Henry.⁴⁰ The proportions are 3–4 atoms strontium to 1 mol. litharge, or 3 atoms zinc, 1 mol. bismuth oxide. With the first mixture the reaction is carried out at 300° C. and 5 atmospheres, or at 200° C. and 10 atmospheres.⁴¹ The catalyst is borne on unsymmetrically perforated discs of porous earth and upon the inner walls of the reaction vessel.

5338. Zinc-Bismuth Oxide Catalyst. A catalyst for the methanol synthesis is composed of a finely ground mixture in the proportions of 1 mol. of bismuth trioxide to 3 of zinc.⁴²

5339. Palladium and Metal Oxides. Catalysts of this type are described and claimed by Storch. The mixtures mentioned are palladium plus chromic oxide, palladium plus zinc oxide, palladium plus cerium oxide. The general description is "a catalyst comprising palladium and a nonreducible metal oxide."⁴³

5340. The Badische Co.⁴⁴ proposes the use, for the methanol synthesis, of catalysts comprising mixtures of copper, silver, gold, zinc, cadmium, or lead, with titanium, vanadium, chromium, manganese, and such cognate elements as zirconium, cerium, thorium, niobium, tantalum, molybdenum, tungsten, uranium, or boron, or compounds of these elements. The catalysts should be free from alkali and from nickel or iron.⁴⁵

³¹ French Pat. 613,896, July 31, 1925, to the same patentees.

³² *Brit. Chem. Abst.*, 1928, 596B.

³³ French Pat. 610,649, Feb. 5, 1926, to Soc. nat. de recherches sur le traitement des combustibles.

³⁴ *Brit. Pat.* 271,452, May 22, 1927, to the I. G.

³⁵ *Cf.* U. S. Pat. 1,698,662 to Mittasch, Müller, Schlecht and Schubart, assigned to the I. G.

³⁶ *Can. Pat.* 251,486, July 7, 1925, to Schmidt and Ufer.

³⁷ *Can. Pat.* 271,569, June 14, 1927, to Gabriel and Brown.

³⁸ *Brit. Pat.* 275,600, Aug. 6, 1926.

³⁹ *Brit. Pat.* 274,492, July 17, 1926.

⁴⁰ *Brit. Pat.* 265,948, Jan. 27, 1927, to Soc. française de Catalyse généralisée (assignees of Henry).

⁴¹ *Brit. Chem. Abst.*, 1928, 473B; *Chem. Age* (London), 1927, 382.

⁴² *Can. Pat.* 276,300, Dec. 13, 1927, to Lefort.

⁴³ U. S. Pat. 1,681,753, Aug. 21, 1928.

⁴⁴ *Brit. Pat.* 229,715, Aug. 23, 1923.

⁴⁵ *Chem. Abst.*, 1925, **19**, 3093.

5340A. For the process described in Brit. Pat. 266,410, Oct. 23, 1925, to Johnson (a Badische Co. patent) the catalysts specified are nickel-coated magnesia or molten iron alloys.⁴⁶

5341. Catalyst in Dust Form.⁴⁷ In one method of hydrogenating heavy oil or synthesizing methanol, the catalyst (e.g., molybdenum-chromium) is maintained as dust suspended in the reaction space.

5342. Similarly, one description⁴⁸ speaks of imparting to the catalyst an irregular whirling movement by the action of the current of entering reactant gases.

5343. Nickel catalyst for methanol synthesis is prepared by Woodruff and Bloomfield⁴⁹ from the hydroxide, oxide, nitrate, oxalate or tartrate by treatment with hydrogen at 500°–600° C. Before reduction the nickel compound may be briquetted with an agglutinant.⁵⁰ Application 279,378 is for an addition to 271,840, which describes methanol catalysts comprising one or more difficultly reducible metal oxides, one or more easily reducible metal oxides, and a metal halide. In an example zinc oxide is added to a solution of chromium nitrate, ferric nitrate and zinc chloride, and the mixture evaporated, heated, and treated with zinc chloride solution.⁵¹

5344. In a process⁵² for the production of oxygenated organic substances, especially methanol, higher alcohols, ketones, and acids, nickel and iron catalysts are used, with other metals and with oxides. Furthermore, sulphur, phosphorus and arsenic are added in some cases. One example given is a catalyst of zinc oxide, chromic acid, ferric nitrate and potassium carbonate; to this is added arsenic pentoxide to combine with any free iron that may be formed (e.g., from the carbonyl). Oxygen is added to the reactant gases to maintain the activity of the contact mass.

5345. The catalysts described in the often cited Badische British Pat. 20,488 of 1913,⁵³ are: 1. Asbestos impregnated with cobalt oxide or osmium oxide with a little caustic soda. 2. A carrier impregnated with potassium carbonate is dried and then soaked in zinc nitrate solution. Catalysts mentioned are cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, zinc, and oxides or other compounds of these metals, and mixtures. It is said to be advantageous to add a basic compound such as an alkali hydroxide.

5345A. Two additions to this patent⁵⁴ describe a modification of the contact mass. The first aims to improve thermal conductivity, thereby avoiding local overheating. Nickel gauze is etched and coated with the active material. (The possible presence of iron carbonyl in the gas is mentioned.) The second addition claims the use of catalytic material containing carbon chemically bound or dissolved. The instances given are carbides of the iron group, partly carburized metals, high carbon steel or cast iron in the form of shavings, etc.

5346. Patart⁵⁵ disclosed as catalysts all those metals, with their oxides and salts, which are known to favor hydrogenation and oxidations.⁵⁶

5347. Methanol Synthesis: Catalysts: Patart Process.⁵⁷ Catalysts for methanol synthesis consist of basic combinations of zinc oxide with metallic oxides of an acid character. The compound should contain at least 2 molecular equivalents of zinc oxide to 1 of the acidic oxide. Basic chromates, vanadates, tungstates and manganates of zinc may be used. In the case of chromates there should preferably be 3 equivalents of zinc oxide to 1 of chromium oxide. Zinc yellow containing sulphate may be used. When sulphur compounds accumulate in the catalyst they may be removed and the catalyst regenerated by heating to redness in an open crucible or by slow circulation through an oxidizing flame.⁵⁸

⁴⁶ Brit. Chem. Abst., Apr. 29, 1927, 316B.

⁴⁷ Brit. Pat. 274,904, July 24, 1926, to the I. G.

⁴⁸ French Pat. 638,109, July 22, 1927, to I. G. Farbenind. A.-G.

⁴⁹ Brit. Pat. applications 279,377 and 279,378, convention date Oct. 25, 1926, assigned to Commercial Solvents Corporation; U. S. Pat. 1,695,447, Dec. 18, 1928, to Woodruff, Bloomfield and Bannister and same assignees.

⁵⁰ Chem. Age, 1927, 17, 579.

⁵¹ Ibid.

⁵² Brit. Pat. 254,760, 1926.

⁵³ Ger. Pat. 293,787. See para. 5399. This patent does not specifically mention methanol.

⁵⁴ Ger. Pats. 295,202 and 295,203.

⁵⁵ French Pat. 540,343, Aug. 19, 1921.

⁵⁶ Ind. Eng. Chem., 1925, 17, 431.

⁵⁷ Brit. Pat. 252,361, May 25, 1925, to Patart.

⁵⁸ Chem. Abst., 1927, 21, 2274.

5348. Bloomfield⁵⁹ prepares a zinc oxide catalyst by igniting moist zinc oxide with traces of ammonia and nitrates, with or without chromium oxide.

5349. The Badische Co.⁶⁰ specifies, as catalysts for the methanol synthesis mixtures of the oxides of copper, silver, zinc, lead and chromium. The method of preparation is given for a mixture of copper and zinc oxides. Hot aqueous solution of copper nitrate (10 mols) and zinc nitrate (1 mol) is precipitated by potassium carbonate. The precipitate is washed and mixed to a paste with 5 per cent of sugar, 30 per cent of formaldehyde (30-40 per cent) and water. The paste is dried and used in a granular form or on an inert carrier. In operation partial reduction of one or both oxides must occur.

5350. Mixed oxides form the catalysts mentioned in one Badische process.⁶¹ Thus: zinc oxide with an oxide of chromium, uranium, vanadium or tungsten; magnesia with molybdenum oxide; ceria with manganese oxide; cadmia with chromium oxide. *The catalysts should be free from iron, nickel and cobalt.*

5351. The Compagnie de Béthune⁶² prepares catalysts for methanol synthesis by depositing formates of metals giving irreducible oxides on a support such as pumice, asbestos, charcoal, or activated carbon. Suitable formates are those of uranium, tungsten, vanadium, zinc, glucinum, chromium, and titanium.

5352. "Suboxides" as Catalysts of Methanol and Synthol Processes. Audibert⁶³ prepared suboxides such as, CrO, V₂O, VO, MoO, WO, U₂O₃, Pb₂O, BiO out of contact with air and found them efficient catalysts in the methanol and synthol syntheses. These suboxides oxidize spontaneously in the air and they must be prepared in the reaction chamber. This is effected by reducing higher oxides in presence of a reduced metal such as copper (which is inert to carbon monoxide) or nickel (which can be removed as carbonyl).

5353. Mixture of Magnesium Oxide and Ferric Hydroxide as Methanol Catalyst. Woodruff and Bloomfield⁶⁴ claim to have discovered a method for utilizing the valuable hydrogenation activity of iron without the usual tendency to form methane. This they effect by making a contact mass composed of magnesia and ferric hydroxide. Favorable proportions are magnesium oxide 750 parts, ferric hydroxide 82 parts. This catalyst is particularly useful in the methanol synthesis.

5354. Mixture of Zinc Oxide and Ferric Hydroxide as Methanol Catalyst. Woodruff and Bloomfield⁶⁵ also recommend a mixture of zinc oxide and ferric hydroxide (750 : 82) as a catalyst in the methanol synthesis.

5355. A group of U. S. patents to Woodruff and Bloomfield⁶⁶ describes mixtures of reducible and "non-reducible" oxides with a metallic halide as producing new and effective catalysts for the methanol synthesis. The special advantages claimed are the reduction of by-product formation and the complete suppression of methane production.

5355A. Patent 1,625,924 deals with mixtures containing: 1. One or more non-reducible metal oxides such as zinc, magnesium, cadmium, chromium, vanadium, tungsten, etc.; 2. One or more easily reducible metal oxides such as copper, silver, iron, nickel, or cobalt, etc.; 3. A metallic halide. The patentees draw attention to the fact that by their method metals of the iron group may be used with advantage though generally excluded because of their tendency to favor the formation of methane.

5355B. Patent 1,625,925 describes catalysts composed of: 1. An oxide of the second group of the Periodic System; 2. An oxide of the third to the seventh group "to serve as a promoter"; 2. A metallic halide. Examples given are: zinc oxide-chromium oxide-zinc chloride; zinc oxide-chromium oxide-vanadium chloride;

Example A

2250 g. of nickel nitrate (Ni(NO₃)₂·6H₂O) are dissolved in 250 liters of water and the solution is heated to 95° C. 7500 g. of zinc oxide are then added with stirring. To this solution there is added sufficient ammonium hydroxide to precipitate the nickel as nickel hydrate. The

⁵⁹ U. S. Pat. 1,668,838, May 8, 1924.

⁶⁰ Brit. Pat. 237,030, Apr. 24, 1924.

⁶¹ Brit. Pat. 227,147 of Aug. 28, 1923.

⁶² Brit. Pat. 274,492, July 17, 1926; *Chem. Age* (London), 1927, 17, 291.

⁶³ *Chimie et industrie*, 1925, 13, 186; *Chem. Abst.*, 1925, 19, 1487.

⁶⁴ U. S. Pat. 1,609,593, Dec. 7, 1926, assigned to Commercial Solvents Corp.

⁶⁵ U. S. Pat. 1,608,643, Nov. 30, 1926.

⁶⁶ U. S. Pats. 1,625,924 to 1,625,929, inclusive, all issued Apr. 26, 1927; Brit. Pat. 272,864, June 21, 1926, covers the same type of catalyst.

precipitated mass is recovered by decantation and filtration, is washed, dried, and broken up into granules.

To this mass is added a solution containing 740 g. of zinc chloride and the mass is again dried.

The hourly yield of condensate is about 1 liter and contains about 30 per cent of methanol.

If the amount of zinc chloride used is doubled, the hourly condensate will be increased to about 2.5 liters and the percentage of methanol will be increased to about 58 per cent.

Substitution of chemically equivalent quantities of magnesium chloride or zinc bromide for the zinc chloride produces similar results.

Example B

4 kg. chromic nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 750 g. nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are dissolved in 5 liters of water. 2.5 kg. of zinc oxide are added with stirring and the mass is heated to dryness and is then further heated till no more nitric oxide fumes are given off, whereby the mixture is transformed to chromic oxide, nickel oxide, and zinc oxide. The resultant mass is broken up into granules and is then moistened with a solution containing 450 g. of zinc chloride. The granules are again dried and are ready for use. If desired, 450 g. of dextrin or a similar agglutinating agent may be added with the zinc chloride, giving firmer granules on drying.

The hourly yield of condensate is about 2.5 liters containing about 58 per cent methanol.

Example C

In place of moistening the granules of the catalyst in Example B with zinc chloride a chemically equivalent amount of chromic chloride may be employed. The results will not be greatly varied. Other mixtures are:

zinc oxide, manganese oxide, magnesium chloride; magnesium oxide, vanadium oxide, magnesium fluoride; magnesium oxide, chromium oxide, chromium chloride; strontium oxide, chromium oxide, zinc chloride; zinc oxide, vanadium oxide, magnesium chloride.

5355C. Patent 1,625,926 reads *verbatim* the same as 1,625,924 till the examples and claims are reached. The second constituent of the catalyst is here, exclusively, nickel oxide. Similarly in 1,625,927 the second constituent is cobalt oxide and, in 1,625,928, copper oxide.

5355D. Patent 1,625,929 describes a catalyst in which the second component is a mixture of the oxides of iron and of chromium.

5355E. The method of preparing these halide-containing catalysts may be gathered from the following example, quoted from U. S. Pat. 1,625,926:

Example D

8 kg. of chromic nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 1.5 kg. of nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are dissolved in 150 liters of water, and to this solution there is added the theoretical amount (5.4 liters of 12.75 normal) of ammonium hydroxide to precipitate chromium hydroxide and nickel hydrate. The solution is then centrifuged to recover the precipitated hydrates and the resultant precipitate is thoroughly washed with water, dried, and broken up into granules.

The resultant granules are moistened with an aqueous solution of 200 g. zinc chloride and again dried, whereupon they are ready for use.

The hourly yield of condensate is about 1 liter, which analyzes about 35 per cent methanol.

5356. The Commercial Solvents Corp.⁶⁷ describe similar catalysts in which one or more difficultly reducible oxides (preferably of a metal of the second group plus an oxide from the third and from the seventh groups as a promoter) has added to it a metal halide. Thus: stir zinc oxide into chromium nitrate solution: evaporate and heat the dry mass until the nitrate is all converted to oxide: mix the product with dextrin solution containing either zinc chloride or magnesium chloride: dry and granulate. Or: a solution of zinc and uranium nitrates is precipitated with potassium carbonate and the dried mass is moistened with zinc chloride and after redrying is granulated. The yield is given for each catalyst.⁶⁸

5357. Two other British patents of Oct. 25, 1926, to Woodruff and Bloomfield, (Commercial Solvents Corp. patents)⁶⁹ deal with the preparation of catalysts for the methanol

⁶⁷ Brit. Pat. 272,864, June 21, 1926, to Commercial Solvents Corp.

⁶⁸ Cf. French Pat. 635,023, May 25, 1927.

⁶⁹ Brit. Pat. 279,377 and 279,378.

synthesis. The first patent describes the making of nickel catalysts in "tablet" form with a binder such as dextrin. The second refers to a method of producing the catalysts described in Brit. Pat. 271,840 and U. S. Pat. 1,625,924, whose essential characteristic seems to be the manipulative detail of treating the crushed mixture of ignited oxides and zinc chloride with aqueous zinc chloride and allowing the mass to harden spontaneously.

5358. United States Pat. 1,558,559, Oct. 27, 1925, to Mittasch, Pier and Winkler, is essentially concerned with the type of catalyst consisting of a mixture of "non-reducible" oxides from different groups of the periodic system with a predominance of the more basic oxide. Oxides from Groups 2 to 7 are suitable: iron and nickel should be excluded. An example given is a mixture of zinc oxide and chromium oxide, from 2 to 12 mols of zinc oxide for 1 mol of chromium oxide. Other examples are: zinc oxide and uranium oxide; zinc oxide and vanadium oxide; zinc oxide and tungsten oxides; magnesia and molybdenum oxide; ceria and manganese oxides.

5358A. British Pat. 229,714, Aug. 23, 1923, covers the same ground. The list of catalysts is very comprehensive.⁷⁰

5358B. This class of catalyst, disclosed in German Pat. 441,433, Sept. 27, 1923, to the same patentees, is available for hydrogenations other than the carbon monoxide-hydrogen syntheses. As catalysts, especially for reduction of carbon oxides, are used in addition to oxide of zinc or cadmium difficultly reducible oxygen compounds of at least two metals of the higher groups of the periodic system. Such mixed catalysts are very resistant to catalyst poisons, and when used in the reduction of carbon oxides yield alcohols almost exclusively. A mixture of 70 per cent of hydrogen and 30 per cent of carbon monoxide at 200 atmospheres passed at 400°–420° over a catalyst containing zinc oxide (1–2 mols.) and chromium trioxide (1 mol.) gives nearly pure methyl alcohol. Addition of alkali hydroxides to the catalyst leads to formation of higher alcohols. Other combinations of catalysts are oxides of zinc, chromium, and uranium or vanadium; cadmium, chromium, and tungsten; zinc, manganese, and vanadium; zinc, vanadium, and uranium; zinc, cadmium, chromium, and uranium. The metals copper, silver, lead, or thorium, or their oxides may be added, but iron compounds are to be avoided. Ethylene is reduced quantitatively to ethane when led with hydrogen at 380°–400° over a mixture of zinc oxide (3 mols.) chromic oxide (2 mols.), and uranium oxide (1 mol.). The reduction of nitrobenzene to aniline, the oxidation of toluene to benzaldehyde and benzoic acid, and of methyl alcohol to formaldehyde, and the preparation of higher alcohols from alcohol, carbon monoxide, hydrogen, and nitrogen, are described.⁷¹

5359. The Brit. Pat. 240,955, July 29, 1924, to Johnson (a Badische patent) discloses no new methanol catalysts, but emphasizes the caution against the presence of nickel or cobalt in the catalyst, and of iron in the walls of the reaction chamber or the gases. It is mentioned that, by adding to the catalyst a small quantity of potassium carbonate, higher alcohols, e.g., propanol, butanol and pentanol are produced. U. S. Pat. 1,569,775, Jan. 12, 1926, to Mittasch and Pier (a Badische patent) covers the same ground.

5360. There is no unanimity about this elimination of iron and its congeners from catalysts for the carbon monoxide syntheses. Thus Wietzel and Speer⁷² describe catalysts suitable for the synthol synthesis, composed of iron, nickel or cobalt. The chief novelty is, however, the incorporation of a small quantity of cadmium or thallium or of their compounds: this addition prevents the deposit of soot on the catalyst. Elements of Group VIII also may be combined similarly with cadmium or thallium. The activity of the catalyst is enhanced by the addition of copper, gold, silver, cerium, zirconium, aluminum, vanadium, uranium, chromium, molybdenum, tungsten, manganese, alkali metals and alkaline earth metals, or compounds of these. But difficultly reducible oxygen compounds of these metals must be absent, or, if present, must constitute not more than 5 per cent of the catalyst material and, preferably, not more than 1 per cent.

⁷⁰ Given fully in *Chem. Abst.*, 1925, 19, 3093.

⁷¹ *Brit. Chem. Abst.*, 1927, 924B.

⁷² Can. Pat. 284,235, Oct. 23, 1928, to Wietzel and Speer, assigned to the I. G.; full abstract in *Chem. Abst.*, 1929, 23, 604.

5360A. Methanol is obtained by passing a mixture of carbon monoxide and hydrogen at high pressure over a mixture of iron oxide or cobalt oxide and oxides of other bivalent metals such as magnesium, manganese, chromium, zinc, beryllium, with or without small amounts of oxides of trivalent metals.^{72a}

5361. Oxide catalysts, such as those used in the methanol synthesis, are rendered mechanically stable by the addition of magnesium sulphate, nitrate or chloride.⁷³

5362. Lazier (assignor to E. I. Du Pont de Nemours) ⁷⁴ prepares special catalysts for the methanol and similar syntheses and for the production of hydrogen from carbon monoxide and steam, and for dehydrogenation. These consist of trivalent chromium compounds and they are obtained by igniting a chromate or dichromate at 600°–1000° C., by prolonged heating to redness of mixtures of chlorides and alkali chromates or dichromates, or by igniting at a red heat a double chromate or dichromate of a metal with ammonia or an organic base such as aniline or pyridine. For the methanol synthesis chromites of zinc, copper, cadmium, magnesium, manganese, silver and iron, or mixtures of these, are suitable.⁷⁵ Lazier ^{76a} also suggests a catalyst comprising a metal oxide such as zinc oxide prepared by subjecting an oxalate to thermal decomposition in an oxidizing atmosphere. U. S. Pat. 1,746,782 relates to the use of a chromite catalyst prepared by calcining at redness a hexavalent chromium salt containing a hydrogenating metal, e.g., zinc chromate. U. S. Pat. 1,746,783 relates to a chromite prepared by igniting a double chromate of ammonium and zinc.

5363. Preparation of Zinc and Chromium Oxide Catalysts. Catalysts of this kind may be prepared by heating a mixture of zinc carbonate or basic zinc carbonate and a chromium compound such as zinc chromate or basic zinc chromate. With zinc chromates the heating must be effected in the presence of reducing gases. A good ratio is one of chromium to 9 of zinc.⁷⁶

5364. Smith ⁷⁷ prepares catalysts for the methanol and similar syntheses from a basic zinc chromate of the formula $4\text{ZnO} \cdot \text{CrO}_3$. This enables the synthesis to be made at 300°–400° C. and the catalyst is not poisoned by sulphur. Volatile compounds (carbonyls) of iron, nickel and cobalt should be excluded.⁷⁸

5365. Catalysts for the production of methanol and other alcohols by interaction of carbon monoxide and hydrogen are prepared by heating a mixture of basic zinc and chromium carbonate. The mixture may be obtained by co-precipitation of a solution of zinc and chromium salts, followed by washing and drying. The catalyst is preferably employed in the pelleted form. If alkali salts are allowed to remain in the catalysts or if additions of such are made, they become suitable for the production of higher alcohols. Examples are given of the precipitation with soda ash solution of (a) a mixture of sodium bichromate or chromate with sulphuric acid to which metallic zinc has been added, (b) the spent electrolyte of a bichromate electrolytic cell, and (c) commercial basic chrome liquor with added zinc sulphate. The proportions of zinc and chromium are preferably so chosen that the precipitate contains 70–80 atomic proportions of zinc to 30–20 atomic proportions of chromium. To regenerate the materials, they are dissolved in sulphuric acid and reprecipitated with sodium carbonate.⁷⁹ Metal oxide catalysts, made by precipitating the metal or metals as carbonates and heating (zinc carbonate at 300°–400°; zinc and chromium carbonates at 250°–300°), also have been used in pellet form.^{79a}

5365A. The Activation of Carbon Monoxide.^{79b} Charcoal does not appear to activate

^{72a} Natta and Faldini, French Pat. 658,788, July 18, 1928; *Chem. Abst.*, **1929**, 5196.

⁷³ Brit. Pat. application 286,284, convention date Mar. 3, 1927, to the I. G.

⁷⁴ Brit. Pat. application 272,555, convention date June 12, 1926.

⁷⁵ *Chem. Age* (London), 1927, **17**, 173; *Chem. Abst.*, 1928, **22**, 1782.

^{76a} U. S. Pats. 1,746,781, -2, -3, Feb. 11, 1930, to E. I. Du Pont de Nemours & Co.; *Chem. Abst.*, **1930**, 1649.

⁷⁶ Brit. Pat. 290,399, Nov. 15, 1926, to Synth. Ammonia and Nitrates, Ltd., and Franklin; *Chem. Age* (London), 1928, **18**, 579; French Pat. 642,318, Sept. 5, 1927, to Imp. Chem. Ind., Ltd.

⁷⁷ Brit. Pat. 275,345, May 12, 1926, to Synth. Ammonia and Nitrates, Ltd., and Smith.

⁷⁸ *Chem. Abst.*, 1928, **22**, 2171.

⁷⁹ Brit. Pat. 293,050, Dec. 23, 1926, to Synth. Ammonia & Nitrates, Ltd., and Franklin; *Ill. Off. Jour.*, Aug. 22, 1928; *Univ. Oil Prod. Bulletin*.

^{79a} Smith, Franklin and Imperial Chem. Industries, Ltd., Brit. Pat. 316,113, Apr. 20, 1928; *Brit. Chem. Abst.*, **1929**, 814B; *Chem. Abst.*, **1930**, 1650. See also French Pat. 672,797, April 8, 1929; *Chem. Abst.*, **1930**, 2140.

^{79b} Jones, *J. Phys. Chem.*, 1929, **33**, 1415–27; *Chem. Abst.*, **1930**, 1275.

carbon monoxide, hydrogen, or oxygen to any appreciable extent, since neither formaldehyde nor methanol can be synthesized from carbon monoxide and hydrogen over charcoal, nor can carbon dioxide be made from carbon monoxide and oxygen over charcoal. Hopcalite activates oxygen but does not activate either carbon monoxide or hydrogen. Apparently carbon monoxide is a better reducing agent than hydrogen by a margin of 30°-50°. Neither iron nor nickel activates carbon monoxide at a point where it reacts with molecular hydrogen. Carbon monoxide must be essentially electropositive in character, since it reacts much more readily with oxygen and chlorine than it does with hydrogen, even when all three of the latter gases are activated. Carbon monoxide reacts only with activated monatomic hydrogen and not with molecular hydrogen, and furthermore it does not react with electronegative hydrogen at a temperature lower than 500°. With calcium hydride at this temperature it gives the same reaction that is produced by carbon dioxide. This work is considered by Jones to support the theory of Fischer and Tropsch (*Chem. Abst.*, 1927, 2065, 2814) for the mechanism of the hydrogenation of carbon monoxide at ordinary pressure.

PREPARATION AND PURIFICATION OF CARBON MONOXIDE

5366. Wietzel treats water-gas or coke-oven gas with steam to convert a part of the carbon monoxide to carbon dioxide and substantially all the sulphur compounds to hydrogen sulphide. The carbon dioxide and hydrogen sulphide are removed (e.g., by water under pressure) and the carbon monoxide is absorbed by ammoniacal cuprous formate solution, from which it can be recovered. The residual hydrogen and nitrogen are utilizable in the ammonia synthesis.

5367. Woodruff⁸⁰ produces carbon monoxide by passing granular carbon downwards through an inclined rotating tube against an ascending stream of carbon dioxide. The temperature of the carbon is kept, by external heating, between 800° and 1500° C.

5368. Purification of Reactant Gases. The Badische Co.⁸¹ describes methods for the exhaustive purification of the water-gas used in the methanol and related syntheses. The removal of organically combined sulphur and of volatile iron compounds is the main objective.

5369. This may be effected by passing through active carbon. In this way not only sulphur compounds but also volatile iron compounds are removed.⁸²

5370. Purification of Water-gas. Water-gas is freed from hydrogen sulphide and then treated with a catalyst, such as silver or gold, which converts the remaining sulphur compounds into hydrogen sulphide, which is then removed.⁸³

5370A. Water-gas and like mixtures are preliminarily purified by treatment with steam in the presence of a catalyst promoting the production of hydrogen and carbon dioxide from carbon monoxide and water. This treatment decomposes organic sulphur compounds in the gas mixture and yields hydrogen sulphide, which is removed with the carbon dioxide. Ger. Pat. 396,115 describes the same treatment applied in the manufacture of methane.^{83a}

5371. Gordon⁸⁴ describes a method of preparing a high-grade water-gas for synthetic purposes. Finely divided fuel is passed with steam through an externally heated vessel constructed of an alloy steel containing a large proportion of chromium or similar addition, such as "Staybrite," "Era/A.T.V.," and "V2A." The fuel may be passed through tubes of such metals, heated by low-grade coal in a similar manner to that of a pulverized fuel boiler furnace. The furnace gases should pass over the tubes at high velocity to secure a high rate of heat transfer. In an example, finely divided coke and steam are blown through a "Staybrite" tube 30 ft. long and $\frac{1}{2}$ in. diameter at about 30 ft. per second, the tube being heated to about 1000° C. A high-grade water-gas containing hydrogen 51 per cent, carbon monoxide 48 per cent, and carbon dioxide 1 per cent is obtained. If air is admitted in addition, a gas is obtained which, after removal of carbon dioxide with steam furnishes the nitrogen-hydrogen

⁸⁰ Can. Pat. 283,913, Oct. 9, 1918, to the Commercial Solv. Corp.

⁸¹ Brit. Pat. 228,959, Aug. 23, 1923.

⁸² Ger. Pat. 462,837, June 28, 1928, to the I. G.

⁸³ Brit. Pat. application 282,634, convention date Dec. 24, 1926, by Fischer; *Chem. Age* (London), 1928, 18, 204.

^{83a} I. G. Farbenind. A.-G. (Wietzel and Winkler, inventors), Ger. Pat. 488,156, April 12, 1923; *Chem. Abst.*, 1930, 2137. Addn. to 396,115.

⁸⁴ Brit. Pat. 282,141, Sept. 11, 1926, to Synth. Ammonia and Nitrates, Ltd., and Gordon.

mixture of the synthesis of ammonia. The process is continuous as distinct from the usual intermittent cycle.⁸⁶

5372. Casale-Sacchi⁸⁶ lays down that for making water-gas free from hydrocarbons, the process is carried out above 1000° C., with excess of steam and at reduced pressure.⁸⁷

5373. Casale-Sacchi⁸⁸ produces hydrogen, hydrogen-nitrogen mixture, or hydrogen-carbon monoxide mixtures according to the following scheme: Carbon monoxide as such or in gases containing it is decomposed completely into carbon dioxide and hydrogen by bubbling through water containing catalysts such as reduced copper, nickel, iron, thallium, platinum, palladium, or metallic oxides or salts of weak inorganic acids, or mixtures thereof, at such a temperature (180°–360°) and pressure (20–150 atmospheres) that the water is kept liquid; thence the gases pass through a heat exchanger to the apparatus for removal of carbon dioxide. Hydrogen or a hydrogen-nitrogen mixture is thus obtained suitable for hydrogenation, the synthesis of ammonia, etc. By modifying the process incomplete catalysis is possible with the production of hydrogen-carbon monoxide mixtures suitable for organic syntheses (methyl alcohol, etc.). The compressed state of the gases is an advantage in the process, and also favors the carbon dioxide elimination.

5374. Mixtures of Hydrogen and Carbon Monoxide.⁸⁹ Vaporized hydrocarbons, or gases containing hydrocarbons (e.g., coal gas), are burnt with just sufficient oxygen at temperatures above 1000° (preferably 1250°–1500°) to convert all the carbon into carbon monoxide. The gas is first given an eddying motion by tangential passage into the lower part of a chamber, whence it expands through an annular passage in to the combustion chamber where the oxygen, as such or in admixture with air, is introduced under pressure through a series of water-cooled nozzles. The hydrocarbons are all converted into carbon monoxide and a small quantity of carbon dioxide; no carbon is deposited. The admission of oxygen is regulated so as to produce the required temperature of combustion; water vapor should be excluded.⁹⁰

5375. Removal of Iron Carbonyl from Methanol. Synthetic methyl alcohol is freed from volatile iron compounds (iron carbonyl) before it is oxidized catalytically to formaldehyde, by passing it, before or after admixture with the air for oxidation, through a tube, 20–80 cm. long, containing inert material, such as glass, quartz, or porcelain, at 150°–300°. The iron carbonyl is decomposed, ferric oxide being deposited. The yield of formaldehyde from methyl alcohol vapor containing 19 mg. of iron as iron carbonyl per liter, is increased from 55.8 per cent to 83–85 per cent, and the life of the catalyst is prolonged considerably, by removal of the iron carbonyl.⁹¹

5376. Carbon Monoxide under Pressure—Necessity of Drying gas.⁹² If not dry the gas will attack the iron of the apparatus below 150° C. Above that temperature special alloys must be used for linings. (Cf. Brit. Pat. 231,285).

5377. Hydrogen is replaced by steam in one of Audibert's processes for the synthesis of hydrocarbons and their oxygen derivatives.⁹³ Carbon monoxide is circulated with steam under heat and pressure over a catalyst composed of a mixture of the oxides of iron and copper.

5378. Apparatus for Methanol Synthesis from Carbon Monoxide and Hydrogen. Apparatus for this synthesis must be made of or coated with a metal or alloy which does not form carbonyls and which can resist the high temperatures used. Iron, cobalt and nickel are excluded. Special steels containing large quantities of chromium, manganese, tungsten, molybdenum or vanadium (such as "steel V2A"), the metals copper, silver, aluminum, and

⁸⁶ *Chem. Age* (London), 1928, 18, 56.

⁸⁷ French Pat. 632,660, Apr. 12, 1927.

⁸⁸ *Chem. Abst.*, 1928, 22, 3497.

⁸⁹ Brit. Pat. 299,492, July 25, 1927; *Brit. Chem. Abst.*, 1929, 17B.

⁹⁰ Brit. Pat. 300,328, Aug. 24, 1927, to Johnson (an I. G. Pat.)

⁹¹ *Brit. Chem. Abst.*, 1929, 45B.

⁹² Ger. Pat. 420,442, Feb. 29, 1924, to the Badische Co., assignees of Bertram and Kuss; *Brit. Chem. Abst.*, 1926, 463B. See also: Brit. Pat. 247,050 and U. S. Pat. 1,631,823 (June 7, 1927), to Jannek, assigned to I. G.

⁹³ Brit. Pat. 247,217, Feb. 6, 1926, to I. G. Farbenind. A.-G.

⁹⁴ French Pat. 639,441, Jan. 24, 1927, to Soc. nat. de recherches sur le traitement des combustibles.

their alloys, also chromium, manganese, tungsten, molybdenum, vanadium may be used. The reaction tube may be protected against the action of hot hydrogen by forming it of a steel jacket with an inner wall of copper or other suitable metal.⁹⁴

5379. In the manufacture of synthetic alcohols the inner parts of the apparatus with which the materials come in contact should consist of, or be coated with, metals other than iron, nickel, and cobalt, or of iron alloys stable to carbon monoxide. The catalysts and gases used must be freed from iron, nickel, and cobalt, and their volatile compounds.⁹⁵

5380. Casale describes the circulation by an injection system of the gases in the methanol synthesis.⁹⁶

5380A. Another process of conducting the methanol synthesis involves bringing the gases under high pressure into contact with a molten metal or alloy (e.g., lead) inert to the gases, baffle plates being arranged in the bath of metal to prevent the gases from coming into contact with the walls.^{96a}

5381. Methanol Synthesis: Apparatus. An arrangement of concentric tubes for heat interchange between reagents and products is described by Casale.⁹⁷

5382. Horizontal tubes containing catalyst are a feature of one apparatus by Patart.⁹⁸

5382A. Brit. Pat. 325,678^{98a} describes a reaction vessel for ammonia or methanol synthesis which is provided with tubes having electric heating elements which are externally adjustable without releasing the pressure in the vessel.

5382B. Undesired side-reactions such as the formation of methane, and the consequent overheating of the catalyst, are said to be avoided by injecting the liquid reaction product continuously, or from time to time, directly into the contact mass.^{98b}

5383. Temperature Control by Injection of Water. The Compagnie de Béthune describes the control of exothermic reaction temperatures by the addition of a volatile liquid, e.g., water. In the methanol synthesis the liquid is injected into the gas mixture just before it meets the catalyst.⁹⁹

5384. In a process due to Walter,¹⁰⁰ hydrogen and carbon monoxide are separated by a diffusion partition formed of catalytic metallized asbestos. The gases diffuse into this partition and react: the product, methanol, emerges under the diffusion pressure.

5385. Heat Regulation and Transfer.¹⁰¹ One invention deals with the utilization of the heat resulting from the reactions between oxides of carbon and hydrogen, or gases splitting off hydrogen, in the presence of a catalyst. Use is made of a steam boiler, in which steam is generated at a pressure of 17 atmospheres, corresponding to a temperature of 205° C. In this boiler there is arranged a number of tubes containing the catalyst, for example, an activated nickel catalyst. A mixture of carbon monoxide and hydrogen is introduced and passed over the catalyst. The heat generated by the reaction serves for the production of steam of 17 atmospheres pressure. In this manner, the production of methane, for example, may be carried on without any interruption by reasons of overheating or through stoppage of the catalytic action as the result of excessive cooling.¹⁰²

⁹⁴ Brit. Pat. 231,285, Feb. 8, 1924, to Badische Co.; *Chem. Abst.*, 1925, **19**, 3490. Cf. analogous patent to I. G. for berginization apparatus. Brit. Pat. 249,155, March 14, 1925; *Chem. Abst.*, 1927, **21**, 1002.

⁹⁵ Brit. Pat. 286,010, Aug. 18, 1926, addition to 240,955, to Johnson, an I. G. communication; *Brit. Chem. Abst.*, **1928**, 473B.

⁹⁶ Brit. Pat. 252,573, July 27, 1925, to Casale.

^{96a} Gordon and Imperial Chem. Ind., Ltd., Brit. Pat. 317,131, May 12, 1928; *Brit. Chem. Abst.*, **1929**, 814B; *Chem. Abst.*, **1930**, 1948.

⁹⁷ Brit. Pat. 252,713, May 28, 1925, to Casale. Similarly Can. Pat. 267,008, Dec. 28, 1926, to same patentee.

⁹⁸ Brit. Pat. 252,362, May 25, 1925.

^{98a} Morgan and Tongue, Feb. 6, 1929; *Chem. Age* (London), **1930**, 400.

^{98b} I. G. Farbenind. A.-G., (Pier, inventor), Ger. Pat. 484,166, Sept. 16, 1923; *Chem. Abst.*, **1930**, 860.

⁹⁹ Brit. Pat. application 283,499, convention date, Jan. 11, 1927; *Chem. Age* (London), **1928**, **18**, 248; French Pat. 639,058, Jan. 11, 1927.

¹⁰⁰ U. S. Pat. 1,685,759, Sept. 25, 1928, to Walter (assigned to Verein für chem. Industrie A.-G.).

¹⁰¹ Brit. Pat. 279,347, May 30, 1927, to Johnson (from I. G. Farbenind. A.-G.). *Ill. Off. Jour.*, Dec. 14, 1927; French Pat. 636,882, July 1, 1927.

¹⁰² *Ind. Chemist*, **1928**, 85.

5386. British Pat. 293,077, Mar. 3, 1927, to Johnson (from I. G. Farbenind. A.-G.) gives a metallurgical method of treating iron to render it suitable for use in the construction of apparatus for chemical processes with hydrogen (oxygen, or sulphur) at high temperatures and pressures.¹⁰³

5387. Protection of Reaction Vessel Wall.¹⁰⁴ In order to prevent diffusion of reducing gases through copper walls of apparatus, owing to reduction of oxide present in the copper, the walls are protected from direct contact with reducing gases by a layer of inert gas such as nitrogen or carbon dioxide. This method is applicable in methanol synthesis.¹⁰⁵ Ordinary steel may be used by operating in the presence of small quantities of substances remaining liquid under the working conditions, e.g., anthracene oil, paraffin wax, or organic compounds of high molecular weight. These substances form a film of liquid on the walls of the apparatus, which is thus protected.^{105a}

5388. Preheating of the Gases. Brit. Pat. application 275,248 by the I. G. (convention date, July 28, 1926), is analogous to Brit. Pat. 192,850, 1921. It describes the preheating of the gases before introduction into the reaction chamber.

5389. Methanol as Internal-combustion Fuel. Methanol, obtained by catalytic hydrogenation of oxides of carbon, is used as a motor (internal-combustion) fuel.¹⁰⁶ It may be mixed with benzol or other fuels.¹⁰⁷

5390. Gaüs and Lappe¹⁰⁸ claim a liquid product obtained by the catalytic hydrogenation of carbon oxides under high pressure and this product with a trace of iron carbonyl, for use as a fuel or ingredient of fuel mixtures. The liquid may be a single aliphatic alcohol or a mixture of aliphatic alcohols.

5391. On the other hand the I. G.¹⁰⁹ describe a fuel for internal combustion engines consisting of gasoline mixed with methanol (which may be the crude synthetic product, preferably anhydrous). As blending agents, benzenoid hydrocarbons or higher aliphatic alcohols or ketones may be added.¹¹⁰

5392. [Calcium Carbide, Coke] and Methanol. Coke is prepared by the carbonization of coal in an oven or retort which communicates directly with a calcium carbide furnace, thus facilitating the introduction of coke into the latter at the highest temperature reached during its formation. The distillation products from the coal are mixed with carbon monoxide and catalyzed under pressure for the production of synthetic methyl alcohol.¹¹¹

5393. In an article by Patart,¹¹² a small-scale plant erected in 1922 by the French "Services des Poudres" is described. The mixture of water-gas and hydrogen is compressed to 500 atmospheres, freed from oily impurities in a simple scrubber, and passed through the catalyst chamber. On leaving this the methyl alcohol produced is condensed by water-cooling and the gases are returned to the process. The condensate is a greenish, turbid liquid, owing to the presence of salts of zinc, copper, and iron, the first derived from the catalyst and the

¹⁰³ *Chem. Age* (London), 1928, **19**, 104.

¹⁰⁴ Brit. Pat. 260,888, June 2, 1926, to I. G. Farbenind. A.-G.

¹⁰⁵ *Chem. Abst.*, 1927, **21**, 3405.

^{105a} I. G. Farbenind. A.-G., Brit. appln. 317,996, appln. date, Aug. 29, 1928; *Chem. Age* (London), 1929, 294. Cf. French Pat. 674,457, May 2, 1929; *Chem. Abst.*, 1930, 2515.

¹⁰⁶ Badische Co., Brit. Pat. 215,776, May 8, 1923.

¹⁰⁷ *Chem. Abst.*, 1924, **18**, 3471.

¹⁰⁸ U.S. Pat. 1,591,526, July 6, 1926, assigned to the Badische Co.; *Chem. Abst.*, 1926, **20**, 3228.

¹⁰⁹ Brit. Pat. 251,969, May 8, 1925.

¹¹⁰ *Chem. Abst.*, 1927, **21**, 1537.

¹¹¹ French Pat., to Patart, 605,530, Oct. 9, 1925; *Brit. Chem. Abst.*, 1926, 812B.

¹¹² *Chim. et Ind.*, 1925, **13**, 179.

last two from the apparatus, and amounting in all to 0.5 g. in 154 cc. The liquid after distillation yields 80 per cent of its original volume of methyl alcohol with traces of acids, higher alcohols, and ammonia, but free from acetone, the remainder being water. Iron, nickel, and cobalt must be excluded, as at temperatures above 300° they catalyze other reactions, such as $2\text{CO} = \text{CO}_2 + \text{C}$, and $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$. They cannot therefore be used in the heating elements of the catalyst chamber. No gas purification such as is necessary in the synthesis of ammonia is required. It is estimated that 100 liters of methyl alcohol can be produced from 300 cu. m. of water-gas at a cost of 25–35 gold francs. At this price, apart from its industrial uses, methyl alcohol is asserted to be capable of competing with gasoline as a motor fuel.

5394. Fermentation Hydrogen. In the production of butyl alcohol and acetone by fermentation, the gases given off contain hydrogen and carbon dioxide which may be used for the synthesis of methanol and formaldehyde.¹¹³

5394A. The process described in this paragraph is the basis of one of the largest methanol synthesis operations, viz., the plant of the Commercial Solvents Corporation at Terre Haute, Ind. An account of this is published by Woodruff.¹¹⁴

The waste gases from the butyl alcohol and acetone fermentation of corn, which are very constant in composition at 6 per cent of carbon dioxide and 40 per cent of hydrogen, are stripped of their solvent vapor content (55 per cent of acetone and 22.5 per cent each of butyl and ethyl alcohols) by passing through cooled activated cocoanut-shell charcoal. After removal of the carbon dioxide, the hydrogen is mixed with air to give a 3 : 1 hydrogen-nitrogen mixture on burning the oxygen to water vapor, and this mixture is then passed to the high-pressure converter. The yield of ammonia is equal to that obtained from the purest electrolytic hydrogen. The high-pressure ammonia plant has been adapted to the production of methyl alcohol, for which purpose it is necessary to remove only a portion of the carbon dioxide content of the fermenter gas, the reaction employed being $\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\cdot\text{OH} + \text{H}_2\text{O}$. Investigations are in progress for the development of a suitable process for supplying carbon monoxide in order to make use of the reaction $\text{CO} + 2\text{H}_2 = \text{CH}_3\cdot\text{OH}$, whereby the methyl alcohol output for a given compressor capacity may be increased 33 per cent.

5394B. In two American works a total of 635 tons of inferior corn is daily converted into about 55 tons of *n*-butyl alcohol, 27 tons of acetone, and 9 tons of ethyl alcohol, while at one of the works 13 tons of methyl alcohol are simultaneously synthesized from the fermentation gases. The corn, containing about 8 per cent of starch, is mixed with water at 71°, sterilized with steam under pressure, and fermented by means of the microorganism *Clostridium acetobutylicum*. The fermentation requires about two and one-half days, and its progress is followed by determining the acidity of the mixture and the gas evolution. The mixture of alcohols and acetone is concentrated and fractionally distilled. The mixture of carbon dioxide (60 per cent) and hydrogen (40 per cent) liberated during fermentation is washed with water under pressure, to bring the proportion to 25 per cent and 75 per cent, respectively, and is then compressed to 300 atmospheres, and passed over a catalyst comprising 97–75 per cent of zinc (or magnesium) oxide with 3–25 per cent of iron hydroxide. From the resultant mixture of 68 per cent of methyl alcohol and 32 per cent of water, pure methyl alcohol is obtained by rectification.¹¹⁵

5395. Synthetic Methanol Produced on Commercial Scale.¹¹⁶ Manufacture of syn-

¹¹³ Brit. Pat. application 268,749, convention date, Apr. 3, 1926, by Commercial Solv. Corp., assignees of Edmonds.

¹¹⁴ *Ind. Eng. Chem.*, 1927, 19, 1147.

¹¹⁵ Tropach, *Brennstoff-Chem.*, 1928, 9; *Brit. Chem. Abst.*, 1918, 281B.

¹¹⁶ *Chem. & Met. Eng.*, 1927, 265. In 1929, the capacity of the plant of the Commercial Solvents Corporation was materially increased, and a unit of the Carbide and Carbon

thetic methanol on a commercial scale has been established at Belle, W. Va., where a plant is being operated by Lazote, Inc., affiliated with the Du Pont interests. Two years of intensive research and experimental work resulted in the development of a purely American process. There has been wide interest in the possible development of methanol in this country and it had been expected American producers would operate under the French or German patents. The plant, operated in conjunction with Lazote's synthetic ammonia manufacture, produces methanol from carbon monoxide and hydrogen under enormous pressures and at high temperatures. The commercial units now in production were built after an experimental plant had been operated satisfactorily for six months. The operations have been so successful that plans have been made to allow for extensive plant expansion.

ADDITIONAL REFERENCES ON METHANOL SYNTHESIS

5396. Elworthy. Synthetic methanol. *Can. Chem. Met.*, 1925, **9**, 139. Review of the Badische, the Patart and the Audibert processes.

5396A. Taylor and Kistiakowsky. Methyl alcohol catalysts. *J. Am. Chem. Soc.*, 1927, **49**, 2468. Study of adsorption of hydrogen, carbon monoxide and carbon dioxide. The methyl alcohol catalysts, zinc oxide and especially zinc oxide mixed with chromium oxide, adsorb very large quantities of hydrogen, carbon monoxide, and carbon dioxide at 0° and 100° after the surface has been cleaned of adsorbed water vapor and carbon dioxide by evacuation at 400° C. The adsorption isotherms are of the type shown by metal catalysts in hydrogenation reactions, but the adsorption capacities are many times those of most metal catalysts under the same conditions. Strong adsorption of hydrogen and of carbon monoxide occurs at very low pressures; relative saturation is attained, since there is little increase in adsorption with a manyfold increase in pressure. This implies a considerable active surface per unit weight of material and a corresponding comparative insensitiveness to poisons. The heat of adsorption exceeds the heat of liquefaction of the gases and reaches values characteristic of heats of adsorption on metal catalysts.¹¹⁷

5396B. Valette. Synthetic methanol. *Chimie et industrie, Special No.* 235 (Apr., 1928). A discussion of the feasibility and probable cost of producing synthetic methanol independently of the ammonia synthesis.

5396C. Voss. New syntheses in the solvent industry. *Kunststoffe*, 1927, **17**, 79, 132, 205. Review of patents for the production of solvents by the carbon monoxide and methane syntheses.

Chemicals Corporation at Niagara Falls began commercial operations. The Du Pont Ammonia Corporation continued its production of methanol, and the future outlook is for greatly increased quantities of this important solvent. *Ind. & Eng. Chem.*, 1930, **22**, 7. In the synthesis of ammonia, a process which has been developed in this country is that of converting into methanol the residual carbon monoxide of the nitrogen-hydrogen mixture thus purifying the latter for ammonia synthesis with the simultaneous production of a valuable product. (Crane, *Ind. & Eng. Chem.*, 1930, **22**, 799.) The Casale process is now being applied industrially at the plant of the "Siri" (Societa Ricerche Industriali) at Terni. The Ammonia Casale and the Societa Terni are said to be jointly interested in this plant. The "Siri" plant is now producing a ton and a half of synthetic methanol daily, which is as much as can be absorbed by the Italian market at present. The plant has a capacity of six tons daily. *Chem. Age* (London), 1930, 24. In Belgium the Société des Fours à Coke E. Coppee is building a works at Villebroek for the manufacture of synthetic methanol. *J.S.C.I.*, 1929, **48**, 1095. The U. S. Trade Commissioner in Tokyo has reported that the Mitsui Mining Co. has obtained permission to use a patent, owned by the Commerce and Industry Department, for the manufacture of methanol on a larger scale. The company has enlarged its plant at Meguro, outside Tokyo, where 200 tons per year have been produced, and the new plans call for a production of at least 1500 tons of methanol per year. *Ind. & Eng. Chem., News Edition*, 1929, **7**, 9. According to Crane, the Du Pont Ammonia Corporation is producing large quantities of higher alcohols by high pressure synthesis from water-gas. These alcohols contain about 80 per cent of butyl and amyl alcohol, the remainder being propyl alcohol and alcohols higher than 5-carbon alcohol. *Ind. & Chem. Eng.*, 1930, **22**, 799.

¹¹⁷ *Brit. Chem. Abst.*, 1927, 1151B.

5396D. Reinders. Composition of water-gas at lower temperatures. *Z. physik. Chem.*, 1927, **130**, 405; *Chem. Abst.*, 1928, **22**, 860. Mathematical treatment of the equilibria under various conditions as applied to the carbon monoxide syntheses.

5397. Horita and Ri. Decomposition of carbon monoxide in presence of reduced nickel. *Bull. Chem. Soc., Japan*, 1928, **3**, 18. A study of the reaction velocity.

5398. Vanick. Deterioration of alloy steels in ammonia synthesis, *Chem. Met. Eng.*, 1927, **34**, 489. A study of the effects of high pressure (100 atmospheres), high temperature (500° C.) and corrosive gases (8.3 per cent ammonia in $N_2 : 3H_2$ mixture), on various alloy steels exposed for ten months.

5399. Audibert. Synthesis of methanol. *Chimie et industrie*, 1928, **20**, 1015. A résumé of Audibert's work, giving his experience with various catalysts. Full abstract in *Brit. Chem. Abst.*, 1929, 162B.

5399A. Bartlett, Hetherington, Kvalnes and Tremearne. The compressibility isotherms of carbon monoxide at temperatures from -70 to 200° and at pressures to 1000 atmospheres. *J. Am. Chem. Soc.*, 1930, **52**, 1374. *Idem.* The compressibility isotherms of hydrogen, nitrogen and a 3 : 1 mixture of these gases at temperatures of -70, -50, -25 and 20° and at pressures to 1000 atmospheres. *Ibid.*, 1930, **52**, 1363.

5399B. Birk and Nitzschmann. The methanol synthesis and its theoretical basis. *Metallbörse*, 1929, **19**, 1350, 1405, 1462, 1573, 1629, 1742, 1798, 1910; *Chem. Abst.*, 1929, 5157. The development of synthetic processes for the production of methanol is outlined, and the fundamental equations for the gas reactions involved are explained fully; 141 such equations, with deductions from them, curves involved, etc., are given. Nitzschmann. Equations and tables of constants involved in the reaction: $CO + H_2O = H_2 + CO_2 + 10,400 \text{ cal.}$ *Metallbörse*, 1930, **20**, 5-6, 118-20; *Chem. Abst.*, 1930, 2365.

5399C. Ullrich. Review of processes for the catalytic production of methanol from carbon monoxide and hydrogen. *Metallbörse*, 1929, **19**, 1181, 1238, 1294.

5399D. Damm, *Mon. prod. chim.*, **11**, No. 114, 1-5; *Chem. Zentr.*, 1928, II, 2208; *Chem. Abst.*, 1929, 4668, has reported on the manufacture of synthetic ethyl and methyl alcohols by the Mining Company of Béthune, from coke-oven gases. The gases consist chiefly of hydrogen, methane, ethylene, carbon monoxide and nitrogen. Hydrogen is separated by liquefaction of the rest of the gases. Ethylene, methane and carbon monoxide can be separated by the same method. Ethylene is converted into ethanol by means of sulphuric acid. A mixture of hydrogen, carbon monoxide and nitrogen serves for the synthesis of methanol. Ammonia is synthesized from the remaining mixture of hydrogen and nitrogen.

5399E. Controversial discussion between Badische Co. and Patart. *Ind. Eng. Chem.*, 1925, **17**, 859.

CHAPTER LIV

REDUCTION OF CARBON OXIDES

II. METHANE

5400. The reduction of carbon monoxide to methane and the reverse reaction are of interest in several connections: the synthesis of methanol, the synthesis of higher oxygenated compounds (synthol), the synthesis of hydrocarbons, in the Cedford gas process, and in the manufacture of hydrogen. We have already discussed the general results of passing hydrogen with carbon monoxide over catalysts in methanating conditions. What follows is a series of notes of specific work on this reaction.

5401. Natural Gas as a Source of Carbon Monoxide. Nash ¹ points out that the natural gas now burning to waste in many places might, perhaps, prove an economical raw material for the carbon monoxide syntheses if treated by a method of the Badische Co.

5402. The Badische Co. states that gases obtained by the distillation of bituminous coal, natural gas or cracking gas can be partially oxidized by passing over a catalyst together with a restricted quantity of oxygen. In some cases, e.g., with natural gas, mixtures were obtained ready for use to be converted catalytically to methanol. In others some adjustment of constituents was necessary. An example is given of a gas mixture derived from coke-oven gas containing carbon dioxide 2 per cent, heavy hydrocarbons 2 per cent, carbon monoxide 7 per cent, hydrogen 52.2 per cent, methane 29.5 per cent, nitrogen 7 per cent, which was mixed with 23 per cent of oxygen and partially burnt with the latter at 1000° C. in presence of nickel-coated magnesia. The resultant gas mixture was carbon dioxide 1.5 per cent, carbon monoxide 26 per cent, hydrogen 64 per cent, methane 3.5 per cent, nitrogen 5 per cent. On many fields natural gas is burned because an economical use has not been, so far, found for it, but the above patent points to the possibility of natural gas being oxidized in the presence of oxygen, afterwards to be reduced in the presence of hydrogen, giving a liquid fuel. Such a method should be far less costly than where the carbon monoxide has to be prepared from coke or semi-coke, particularly as tremendous quantities of natural gas in various parts of the world are at present going to waste.²

5403. The Reduction of Carbon Monoxide to Methane in the Presence of Iron and under Pressure. This reaction was studied by Fischer and Tropsch.³ The apparatus was an iron tube 90 cm. long and 2.1 cm. internal diameter. The tube was electrically heated. The conditions were: pressure, 2-100 atmos-

¹ Possible auxiliary sources of liquid fuels: *J. Inst. Petrol. Tech.*, 1924, **13**, 681. Refers to Badische Co.'s Brit. Pat. 266,410.

² The subject of the utilization of methane is well and fully examined by Nash and Stanley, *J.S.C.I.*, 1929, **48**, 2T, and in *Fuel in Science and Practice*, 1928, **7**, 397. See also Nash on "Synthetic Fuels," *J. Inst. Petroleum Tech.*, 1930, **16**, 313.

³ *Brennstoff-Chem.*, 1923, **4**, 193-197; *Chem. Abst.*, 1924, 349.

pheres; temperature 400°–430° C. The gas mixture consisted essentially of carbon monoxide and hydrogen. At 2 atmospheres the yield of methane was small. The greatest yield was at 45–55 atmospheres. The reaction may be considered as taking place as follows:



5404. Reduction of Carbon Monoxide to Methane with Metal Catalysts.⁴ The metals catalyzing the reduction of carbon monoxide to methane in order of decreasing efficiency, are ruthenium, iridium, rhodium, nickel, cobalt, osmium, platinum, iron, molybdenum, palladium, and silver. Copper, gold, tungsten, antimony, manganous oxide, and chromic oxide are without influence. Since no carbonyls of osmium, iridium, palladium, or rhodium are known, it cannot be definitely stated that the formation of a metal carbonyl is a stage in the reaction. Similarly, no relation can be traced between the affinity of the metal for hydrogen and its efficiency as a catalyst. No intermediate products likely to be formed, such as formaldehyde, etc., could be isolated, but unsaturated hydrocarbons were observed with ruthenium and platinum which cannot be accounted for. Ruthenium is also active in the reduction of carbon dioxide to methane; although poisoned by sulphur compounds, it is reactivated by heating at 600°–700° in a current of air. Oxides such as aluminum oxide in conjunction with nickel have a beneficial catalytic influence.⁵

5405. Reduction of Carbon Monoxide—the "hot-cold" Tube. The hot-cold tube consists of an electrically heated iron spiral brought to red heat in an iron autoclave surrounded by cold water. When this apparatus was filled with a mixture of carbon dioxide 15, carbon monoxide 23 and hydrogen 56 at 120–150 atmospheres, the pressure fell to 70–80 atmospheres and the gas mixture was found to contain methane hydrocarbons 15–19 per cent, carbon dioxide 9 per cent, carbon monoxide 40 per cent, hydrogen 22–29 per cent. Carbon was deposited on the spiral and water formed contained formaldehyde. When the temperature of the spiral was controlled and held at about 620° C., the hydrogen disappeared almost completely; a larger quantity of saturated hydrocarbons and an acid aqueous solution containing formaldehyde were formed. The only effect of treating the spiral with alkali was to decrease the yield of formaldehyde.⁶

5406. The results obtained by Fischer and Jaeger have been confirmed with various binary and ternary mixtures of carbon monoxide, carbon dioxide, and hydrogen. Reduction is perceptible at 500°, and is accelerated by higher temperatures and pressures. Covering the iron spiral with asbestos or with aluminum hydroxide had little effect. Methane is formed in amounts up to 30 per cent, and is accompanied by higher homologs. Formaldehyde was only detected qualitatively, and methyl alcohol was not formed. Appreciable amounts of carbon were deposited. On replacement of the iron spiral by a copper spiral or foil, partial reduction of carbon dioxide to carbon monoxide was observed only at 800°; at lower temperatures no reaction occurred. Nickel wire gives similar results to iron, but the reaction is slower. Tungsten, molybdenum, and charcoal behave similarly about 550°, but the reaction velocity is considerably less than in the case of iron and nickel.

5407. When heated at 600°–700° and under 1–6 atmospheres in the hot-cold tube previously described in presence of steam and iron, carbon monoxide is decomposed into carbon dioxide and carbon and into carbon dioxide and hydrogen, the former reaction preponderating. The same reactions occur in the presence of methane, the latter gas being practically unchanged. Mixtures of carbon dioxide and methane are practically unchanged under these conditions. Methane alone is practically unchanged, only traces of carbon being deposited and a very little hydrogen formed, although condensation to form higher homologs may occur. Unsaturated hydrocarbons, formaldehyde, or alcohols were not formed.⁷

5408. Reduction of Carbon Monoxide—Nickel Catalyst: Atmospheric Pressure. The normally quantitative methane formation from carbon monoxide (1 volume) and hydrogen

⁴ Fischer, Tropsch and Dilthey, *Brennstoff-Chem.*, 1925, **6**, 265.

⁵ *J. Chem. Soc.*, 1925, ii, 982.

⁶ Fischer and Jaeger, *Abhandl. Kennt. Kohle*, 1925, **7**, 68; *Chem. Abst.*, 1927, **21**, 2550.

⁷ Fischer and von Wangenheim, *Brennstoff-Chem.*, 1928, **9**, 94–97; *Brit. Chem. Abst.*, 1928, 355B.

(3 volumes) over a nickel catalyst at 240°–250°, is much inhibited by the presence of ammonia. The final gas contained methane 13 per cent; there was no formaldehyde or hexamethylene-tetramine. With a nickel catalyst which had been treated with alkali the same mixture at 400° C. gave 53 per cent of methane and 1.1 per cent of saturated hydrocarbons; water was also formed. With untreated catalyst no saturated hydrocarbons were formed. An equal volumes mixture of hydrogen and carbon monoxide over an alkaline nickel catalyst deposited much carbon at 400° C. The more alkali the less carbon dioxide and methane were formed. No methanol was detected.⁸

5409. The optimum temperature for the formation of methane is in a narrow zone at 250° C. A copper-nickel catalyst gives poor yields. Palladium does not cause the formation of ethylene. No formaldehyde was formed as the result of passing carbon monoxide, hydrogen chloride and hydrogen over cuprous chloride, copper, iron or nickel at 200°–300° C. (which is contrary to the statement by Church in French pat. 519,849). Formaldehyde is formed when formic acid vapor mixed with hydrogen is passed over metals at lower temperatures, over indifferent substances at higher temperatures or through an empty glass tube at 700°–750°. Carbon monoxide and steam yield small quantities of formic acid when passed over hydrated silica at 320° C.; at 450° C. in a quartz tube about 1.5 per cent of the carbon monoxide is converted into formaldehyde. The yield decreases with increasing temperature; no formation of formaldehyde occurs in the presence of nickel or copper catalysts or when steam is replaced by hydrogen. Hydrogen freed from hydrogen sulphide does not reduce carbon monoxide to formaldehyde at 400° C., nor is formaldehyde produced by reducing the compound $K_3Fe(CN)_6CO$ with hydrogen.⁹

5410. Catalytic Formation of Methane from Carbon Monoxide and Hydrogen.¹⁰ A sugar charcoal-nickel (73/27) catalyst for the reaction $CO + 3H_2 = CH_4 + H_2O$, prepared by the carbonization of a mixture of solutions of sucrose and nickel acetate, retains its activity undiminished for months when the theoretical ratio of carbon monoxide and hydrogen is employed. The critical space velocity (cubic centimeters of gas per cubic centimeter of contact material per minute) below which carbon monoxide is found in the outflow gases is large, and increases considerably with rise of temperature. This catalyst entirely suppresses the reaction $2CO = C + CO_2$, and prevents the deposition of carbon on the nickel surface. Ceria acts as a promoter for the catalyst, e.g., at 355° the critical space velocity is 3.5 without ceria, whereas with ceria it is >4.4. The presence of carbon dioxide in the outflow gases is due mainly to the reaction $2CO + 2H_2 = CO_2 + CH_4$, and partly to the reaction $CO + H_2O = CO_2 + H_2$, the latter being suppressed at high space velocities.

5411. Production of Fuel Gases Rich in Methane.¹¹ The sugar charcoal-nickel catalyst is not efficient in the conversion of hydrogen-carbon monoxide mixtures (1 : 1) into methane in accordance with the equations $2CO + 2H_2 = CO_2 + CH_4$ and $CO + 3H_2 = CH_4 + H_2O$, unless a promoter be used. Ceria is without influence in promoting the first reaction, but vanadic acid is very efficient, its activity rapidly increasing with rise of temperature. The activity of this catalyst remains steady for months if the reaction temperature be maintained below 500°, and at 400° the exothermic reactions involved maintain the temperature of the catalyst without external heating. Ferric oxide is also an efficient promoter, but the substitution of coconut charcoal for sugar charcoal yields a catalyst which, although possessing initial high activity, does not remain steady, and has a small temperature coefficient. Examination of the composition of the incoming and effluent gases shows that equivalent quantities of methane and carbon dioxide are produced by the first reaction, the excess of methane found resulting from the second reaction which is favored by a high space volume. The calorific value of the resulting gas is slightly lower than that of carburetted water-gas, the large volume of carbon dioxide produced acting as a diluent.¹²

5412. The effects of various catalysts, mostly mixed metallic hydroxides, for the reaction $2CO + 2H_2 = CH_4 + CO_2$ have been studied, and it is found that while some of them, e.g., nickel hydroxide on aluminum hydroxide, are active at 300°, they are not steady, and the rate of fall of activity is rapid. The sugar charcoal-nickel catalyst on pumice is more

⁸ Tropsch, Schellenberg and von Philippovich, *Abhandl. Kennt. Kohle*, 1925, 7, 63; *Chem. Abst.*, 1927, 21, 2550.

⁹ Jaeger and Winkelmann, *Abhandl. Kennt. Kohle*, 1925, 7, 55; *Chem. Abst.*, 1927, 12, 2550.

¹⁰ Chakravarty and Ghosh, *Quart. J. Indian Chem. Soc.*, 1925, 2, 150.

¹¹ Chakravarty and Ghosh, *Ibid.*, 157.

¹² *Brit. Chem. Abst.*, 1925, 948B.

active if 50 per cent more nickel is used in its preparation and, in contradistinction to the others used, loses its activity very slowly.¹³

5413. Methane by Reduction of Carbon Monoxide—Nickel Catalyst. This well-known reaction is the subject of British Pat. 244,076, Dec. 3, 1924, to the Chem. Fabr. Griesheim-Elektron. The gas-flow is adjusted to insure rapid removal of the product from the reaction zone.¹⁴

5414. Chemicals, in the technical number, Mar. 15, 1926, speaks of this patent (or application), as follows: The Chemische Fabrik Griesheim-Elektron has applied for a British patent for a process in which methane is prepared by the interaction of carbon monoxide and hydrogen-containing gases over a nickel catalyst maintained at a temperature of 400° C. or above. To permit of the use of this temperature, which is substantially higher than that usually employed, the rate of flow of the gas mixture is adjusted to insure rapid removal of the product from the reaction zone. The gases may be passed over one or more catalysts arranged in series, or the process may be operated cyclically.

5415. The Decomposition of Carbon Monoxide on Nickel. H. A. and T. Bahr¹⁵ by experimental and analytical methods seem to have proved that metallic nickel catalyzes the reaction: $2\text{CO} = \text{C} + \text{CO}_2 + 39.9 \text{ cal.}$, by first forming a carbide Ni_3C . Below 270° C. the decomposition of the monoxide with formation of Ni_3C goes to completion, without deposit of free carbon and then stops. Between 270° C. and about 400° C. decomposition continues, the catalyst being Ni_3C and free carbon is deposited. Above 400° C. the carbide decomposes. By passage of hydrogen over the catalyst the carbon of the Ni_3C comes off as methane, but the free carbon is unaffected.

5416. Synthesis of Methane.¹⁶ Hydrogen and carbon monoxide are passed over a nickel catalyst at a temperature above 500° C. and at a speed rapid enough to prevent separation of carbon.

5416A. Carbon monoxide is caused to react with a hydrogen-containing gas in successive stages to form formaldehyde, methanol and then methane, without isolating intermediate products and at least one of the first two stages of the reaction is effected in the presence of "mild" reduction catalysts such as copper, manganese, cadmium, zinc, lead, tin, magnesium, silver, gold or platinum associated with oxidation catalysts such as compounds of chromium, vanadium, titanium, molybdenum, tungsten, cerium, thorium, uranium or zirconium, both of which are incorporated in porous carriers such as pumice or kieselguhr of not more than slight catalytic activity; the stage producing methane from methanol is effected in the presence of strong reduction catalysts such as iron, nickel, cobalt, or palladium. U. S. Pat. 1,741,307 relates to processes in which, in at least one of the first two stages, the oxidation catalyst serves as a carrier for the "mild" reduction catalyst. U. S. Pat. 1,741,308 specifies the admixture together of the catalysts for the different successive stages of the process.^{16a}

5417. Randall and Gerard examined the synthesis of methane from carbon dioxide and hydrogen.¹⁷ The equilibrium for the reaction: $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$ was determined by the dynamic method, at atmospheric pressure and at temperatures between 322° and 392.5° C. Hightower and White^{17a} report experimental work on the same equilibria.

5418. Conversion of Methane into Hydrogen and Carbon Monoxide. The effect of 20 different catalysts on the reaction $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ at 850° C. has been studied. Copper, iron, molybdenum, and tungsten had a negligible catalytic effect; cobalt and nickel were equally active, giving a 50 per cent conversion under the experimental conditions, but their activity was greatly increased by the addition of alumina, a nickel-alumina catalyst giving a 95 per cent conversion. Porous pot proved to be the most suitable support for the catalyst, other materials breaking down after a time.

5419. By mixing a purified coke-oven gas with carbon dioxide in the proportion 4 : 1 and passing the mixture over one of the more active catalysts at 850°-870° C., the methane was almost completely converted into hydrogen and carbon monoxide. At the same time the unsaturated hydrocarbons were completely decomposed and the organic sulphur com-

¹³ *Idem, ibid.*, 1927, 4, 431.

¹⁴ *Chem. Abst.*, 1927, 21, 104.

¹⁵ *Ber.*, 1928, 61B, 2177; *Chem. Abst.*, 1929, 23, 756.

¹⁶ U. S. Pat. 1,643,663, Sept. 27, 1927, to Klatte and Sol.

^{16a} Jaeger (to Selden Co.), U. S. Pats. 1,741,306, -7, -8, Dec. 31, 1929; *Chem. Abst.*, 1930, 1125-6. Cf. U. S. Pat. 1,735,925, Nov. 19, 1929; *Chem. Abst.*, 1930, 695.

¹⁷ *Ind. Eng. Chem.*, 1928, 20, 1335; *Chem. Abst.*, 23, 814.

^{17a} *Ind. Eng. Chem.*, 1928, 20, 10.

pounds were converted into hydrogen sulphide. By the passage of a mixture of coke-oven gas and water vapor over the same catalysts at 860°–930° C. the reaction $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ was made to proceed almost to completion, and a gas was thereby obtained of composition suitable for the benzene synthesis. It was not possible to bring about a complete decomposition of the methane by passage of this mixture over heated coke, even at 1000° C. with a large excess of water vapor and a slow rate of passage of the gas.¹⁸

5419A. Hydrocarbons and other organic compounds are prepared by treating oxides of carbon with hydrogen at a high temperature in the presence of catalysts which contain besides metals of the 8th group of the periodic system, alkali metal compounds, the content of alkali metal (in the combined state) being below 0.6 per cent.^{18a}

5419B. Paraffin hydrocarbons containing a plurality of carbon atoms are prepared from hydrogen and oxides of carbon by passing these gases over a catalyst at a temperature lower than that at which the catalyst promotes the production of methane only. The reaction may be conducted at reduced, ordinary, or slightly raised pressure. Suitable catalysts are mixtures of zinc oxide with iron, or copper with iron, or cobalt with copper; pure nickel is not considered suitable.^{18b}

VARIOUS SYNTHESSES OF HYDROCARBONS

5420. Methane or a gas containing it is heated at 200°–600° under pressure with a catalyst, e.g., ferric oxide, mixtures of metallic oxides, or the corresponding metals obtained by reduction of the oxides. Liquid hydrocarbons are obtained, the greater part of the product distilling between 38° and 100°. Butane and ethane are also produced. The methane used need not be pure, the presence of hydrogen, oxygen, or other gases appearing favorable to the reaction.¹⁹

5421. According to the Compagnie de Béthune²⁰ it is necessary to have oxygen present in order to produce petroleum hydrocarbons from methane; this oxygen may be in the form of oxide catalysts.

5422. Methane or methane-containing gas is cracked at 500°–950° C., cooled, and at about 250°–350° C. is conducted over a catalyst containing zinc chloride; both operations are conducted under a pressure of not less than 70 atmospheres.²¹

5423. Referring to such a process, Goudet²² discloses the passage of the gas at the higher temperatures over calcium fluoride, to which may be added sulphides, selenides, or tellurides.

5424. Goudet also²³ says methane may be treated with nickel, iron or cobalt, or their compounds under a pressure of 1000 kg. per sq. cm.: the reaction is promoted by the addition of alkali or alkaline earth metals or of chlorine, bromine, iodine, sulphur, selenium or thallium. The methane may be mixed with mercury vapor and subjected to an electrical field.

5424A. Methane, mixed with steam, is injected at 400 lb. per sq. in. into a retort initially at 1260°, and the mixture of carbon monoxide and "nascent" hydrogen is passed at 325°–475° through a catalyst chamber containing iron calcined with potash. The resultant mixture of alcohol and hydrocarbon vapors passes through a relief valve to cooling coil and receiver. Alternate use of a similar retort in parallel with the first and connected with the same catalyst chamber gives a continuous process.^{24a}

5425. To produce hydrogen and hydrocarbons (mainly olefinic), a thin stream of methane is gradually and uniformly heated and the reaction products are cooled suddenly and kept under reduced pressure until completely cooled. The stream may be of annular form, of about 1 mm. thickness and may be heated to 950° C. under a reduced pressure of 20 cm. Hg.²⁴

¹⁸ Fischer and Tropsch, *Brennstoff-Chem.*, 1928, 9, 39; *Brit. Chem. Abst.*, 1928, 322B.

^{18a} I. G. Farbenind. A.-G., French Pat. 660,133, Sept. 10, 1928; *Chem. Abst.*, 1930, 127.

^{18b} Fischer and Tropsch, Ger. Pat. 484,337, July 22, 1925; *Chem. Abst.*, 1930, 1119. Cf. U. S. Pat. 1,746,464, Feb. 11, 1930; *Chem. Abst.*, 1930, 1649.

¹⁹ French Pat. 613,542, July 27, 1925, to Comp. de Béthune; *Brit. Chem. Abst.*, Feb. 17, 1928, 116B.

²⁰ French Pat. 615,972.

²¹ Brit. Pat. 255,493, July 18, 1925.

²² French Pat. 31,758, Dec. 9, 1925 (addition to French Pat. 613,146).

²³ French Pat. 32,666, May 26, 1926 (addition, also, to 613,146).

^{24a} Webster, U. S. Pat. 1,711,913, May 7, 1929; *Brit. Chem. Abst.*, 1929, 880B.

²⁴ *Chem. Abst.*, 1927, 21, 3368; Brit. Pat. 261,267, Apr. 29, 1926, to Pétrole synthétique S. A. and Folliet.

5426. Indirect Synthesis of Hydrocarbons from Methane.²⁵ Carbon deposited in a heated retort by the passage of methane through it is decomposed by a current of steam, yielding carbon monoxide and hydrogen, and the gas mixture after the addition of more hydrogen, is used for the synthesis of hydrocarbons.²⁶

5426A. Carbon Black.^{26a} Methane is thermally decomposed by passing it with a diluent such as nitrogen or hydrogen through a retort containing highly heated checkerwork to obtain a carbon of black color and low rubber stiffening qualities.

5427. Alcohols and Liquid Hydrocarbons from Coal Gas.²⁷ Coal gas, or a suitable mixture of hydrogen, methane, and carbon monoxide, is led at 400°–600° C. under 400 atmospheres over magnetic iron oxide, and the gaseous products, after condensation of alcohols, etc., are converted into oily hydrocarbons, boiling-point below 100° C. by passage over active carbon at 100°–400° C.²⁸

5427A. Ferric oxide, unlike reduced iron, yields liquid as well as gaseous products when used as a catalyst for the interaction of carbon monoxide and hydrogen. The yield of liquid products quickly falls to zero with the reduction of the ferric oxide. The reduction of the ferric oxide is prevented to some extent by the addition of alkali, or by the use of a gas mixture containing excess of hydrogen. The addition of alkali salts, or copper, is of no benefit, neither is the use of lower pressures and temperatures practical, nor the replacement of the iron by manganese. In all these cases carbon is deposited on the catalyst, and leads to irregular action. Better results have been obtained by converting the ferric hydroxide into phosphate or borate by addition of acid, adding a solution of the nitrates of copper and manganese, precipitating as a paste by soda, and then adding potassium carbonate. With this no carbonaceous deposit is formed, and a yield of 15–17 per cent by weight of organic liquids has been obtained. The remainder is gaseous hydrocarbons, carbon dioxide, and water vapor. About two thirds of the organic liquid distill below 180°, this including a large proportion of aliphatic alcohols which must be recovered from the aqueous layer. These results were obtained at 380°–450° with a space velocity of about 10,000 and at 150 atmospheres pressure.^{28a}

5428. In one of Patart's processes²⁹ another method for the simultaneous synthesis of methanol and liquid hydrocarbons is adopted. A mixture of coal gas and water-gas in approximately equal amounts is used, a typical sample having carbon dioxide, 3 per cent; carbon monoxide, 26 per cent; ethylene, 1.4 per cent; methane, 8.9 per cent; hydrogen, 54 per cent; oxygen, 0.6 per cent; nitrogen, 6 per cent. This is circulated for eight hours at 150–250 atmospheres over a zinc oxide-chromium oxide catalyst at 300° C., fresh gas being introduced as required. The liquid product is a mixture of 2.5 per cent hydrocarbons and hydrated methanol. The spent gas contains: carbon dioxide, 1.2 per cent; carbon monoxide, 27.2 per cent; ethylene, 2.2 per cent; methane, 27.3 per cent; hydrogen, 16.7 per cent; nitrogen, 25.4 per cent; oxygen, nil. It is claimed that the hydrocarbons are formed from the ethylene, while the methanol is produced by the hydrogenation of the acids of carbon in the gas and subsequently from the same substances formed by the incomplete combustion of the methane. At higher pressures the reaction can be taken to a final hydrogen concentration of 4–5 per cent.

5429. Synthesis of Benzene Hydrocarbons from Methane under Ordinary Pressures and without Catalysts.³⁰ The yields of tar and light oil formed when methane is passed through a heated tube have been determined. A relatively high temperature (above 1000°) and a high gas velocity are necessary to obtain satisfactory yields of liquid products. The formation of free carbon increases rapidly with rise of temperature, but can be prevented or diminished by correspondingly increasing the gas velocity. Quartz and porcelain are the most suitable materials for the tube; iron and copper favor the separation of carbon. Up

²⁵ Can. Pat. 264,324, Nov. 28, 1925, to Spear, assigned to Thermatomic Carbon Co.

²⁶ Brit. Chem. Abst., 1927, 961B.

^{26a} Spear and Moore (to Thermatomic Carbon Co.), Brit. Pat. 307,743, March 12, 1928; Chem. Abst., 1930, 212; Brit. Chem. Abst., 1930, 626B.

²⁷ French Pat. 613,541, July 27, 1925, to the Cie. de Béthune.

²⁸ Brit. Chem. Abst., 1928, 885 B.

^{28a} Audibert and Raineau, Ann. Off. nat. Combustibles liquides, 1928, No. 3; Ind. Eng. Chem., 1929, 21, 880–885; Brit. Chem. Abst., 1929, 840B.

²⁹ Brit. Pat. 247,932, Apr. 21, 1926; J. Inst. Petrol. Tech., June, 1927, Abst. No. 285; Univ. Oil Prod. Co. Bull.

³⁰ Fischer, et al., Brennstoff-Chem., 1928, 9, 309.

to 12.9 per cent of the methane has been converted into light oil and tar by one passage through a heated quartz tube. If the methane is diluted with other gases a higher reaction temperature is necessary in order to bring about the same percentage conversion. The tar contains considerable quantities of naphthalene; the presence of anthracene and phenanthrene has also been established. The light oil consists principally of benzene and toluene.³¹

5430. A process for making benzenoid hydrocarbons is described³² in which methane or methane-containing gas is conducted over a catalyst at 700°–1000° or higher, at ordinary pressure or higher at sufficiently high velocity to prevent condensation of the primary products into higher molecular products.³³

III. OTHER HIGH-PRESSURE SYNTHESIS OF HYDROCARBONS AND SYNTHOL

5431. Certain modifications in the operative conditions, chiefly of the catalyst composition, produce from mixtures of carbon monoxide and hydrogen, instead of methanol, its higher homologs and other oxygenated compounds and, instead of methane, higher hydrocarbons, saturated and unsaturated.

5432. Two distinct methods of operation are followed: high-pressure operation which dates from 1913 at latest, and low (atmospheric) pressure operation which was introduced by Fischer and Tropsch in 1926.

5433. There has so far been much less commercial development of these processes than of the related methanol process. For this there are two reasons. Neither process gives, at a cost which can more than meet the competition of established methods, a preponderant yield of a single utilizable chemical, analogous to methanol, for which there is a large demand. Secondly, their products in the most immediately obvious field of utilization, viz., the fuel market, have to compete with an enormous output of cheap natural products in a closely organized trade.

5434. Synthol and Synthin. The mixtures of oxygenated compounds obtained by the reduction of carbon oxides under suitable conditions are known as *synthol* which convenient name was given to them by Fischer.³⁴ The mixtures of hydrocarbons produced by a further modification he calls *synthin*.

5435. The Badische Company's patents of 1913 and 1914³⁵ are justly regarded as the starting-point of the high-pressure processes for the synthesis from carbon oxides and hydrogen of the homologs of methane and ethylene and their oxygenated derivatives. The British patent is cited *verbatim* in Fischer's *Conversion of Coal Into Oils* (tr. Lessing: Van Nostrand Co., 1925): the following abstract gives the substance of the corresponding French patent.

5436. Carbon monoxide or dioxide, or a mixture of the two, is made to react with hydrogen or compounds rich in hydrogen, such as methane, by passing the gases over heated catalysts under high pressure. According to the nature of the catalyst and the pressure employed, a variety of products may be obtained, such as liquid hydrocarbons, both saturated and

³¹ *Brit. Chem. Abst.*, 1928, 844B.

³² *Brit. Pat.* 264,827, Jan. 19, 1926, to the I. G.

³³ *Brit. Pat.* 258,608 and *French Pat.* 610,543 relate to the same class of operations. None of these patents gives any clear statement of yield; *Univ. Oil Prod. Co. Bull.*

³⁴ *Brennstoff-Chem.*, 1923, 4, 276.

³⁵ *Brit. Pat.* 20,488, Sept. 10, 1913; *Ger. Pat.* 293,787; *French Pat.* 468,427, Feb. 13, 1914, convention date, Mar. 7, 1913; *U. S. Pat.* 1,201,850, Oct. 17, 1916, this last to Mittasch and Schneider.

unsaturated, aldehydes, alcohols, ketones, and acids. To obtain larger quantities of liquid product it is better to use gaseous mixtures containing relatively small proportions of hydrogen. Metals or metallic oxides (cerium, cobalt, molybdenum, osmium, palladium) may be used as catalysts, and their effect may be intensified by adding highly basic substances, such as alkali hydroxides. A mixture of two parts of pure carbon monoxide to one part of pure hydrogen passed over asbestos impregnated with cobalt oxide and a small quantity of caustic soda, heated to 300°–400° C., under a pressure of 100 atmospheres, yields a deposit of carbon, together with water, carbon dioxide, methane, and higher hydrocarbons and their oxygen compounds, which are condensed or absorbed in a cooled vessel. The condensed liquid consists of an aqueous solution of aldehydes, etc., on which floats an oily liquid containing saturated and unsaturated hydrocarbons, of boiling-points up to 250° C. or more. If a gaseous mixture containing nitrogen or sulphur compounds is used, compounds containing nitrogen and sulphur are formed in some cases. Gaseous mixtures which contain traces of substances which act as contact poisons are purified by passing them over a heated mass of catalyst before bringing them to the reaction proper.³⁶

5437. In the light of more recent knowledge, one is interested by the mention of the use of the alkaline catalysts, of the possible though not recommended low working pressure of 5 atmospheres, of the insistence on the carbon monoxide being in excess, even to three times the volume of the hydrogen. Fischer (*loc. cit.*, p. 222) was unable to confirm the statement that a zinc oxide catalyst with potassium carbonate at 90 atmospheres and 400° C. causes the production of liquid hydrocarbons and organic oxygenated compounds. He found it necessary to add a metal.

5438. Mechanism of Synthol Formation—Condensation of Methanol. With a view to elucidating the synthol reaction Tropsch and von Philippovitch³⁷ investigated the condensation of methanol in the presence of the catalysts used in the production of synthol. In nearly all cases a small quantity of oil of terpene-like odor was obtained and the possibility of the formation of higher-boiling compounds was proved. With sodium methoxide, methyl ether was formed and the residual gas was composed almost exclusively of hydrogen. In all other cases considerable quantities of methane were produced. With an alkali iron catalyst oily products were obtained proving possible the production of oils direct from methane.

5439. Patart³⁸ passes mixtures of water-gas and gaseous hydrocarbons over hydrogenation catalysts, e.g., nickel, silver, copper, iron, at high pressures and at 300° to 600° C. for the production of alcohols, aldehydes and acids. The pressure was between 150 and 200 atmospheres.

5440. A similar or identical process producing chiefly higher alcohols, ethers and ketones,³⁹ is also described by Patart. The process is cyclic and carbon dioxide is eliminated, the synthetic products being condensed. The apparatus and method of working are described in detail. The catalysts used are silver, copper, zinc, manganese, molybdenum, uranium, vanadium and a combination of alkali or alkaline earth oxides of acid character, e.g., chromates, manganates, molybdates, tungstates, uranates and vanadates of sodium, potassium, rubidium and barium.⁴⁰

5441. Patart⁴¹ describes other catalysts for producing synthol. Catalysts for the reduction of carbon monoxide or carbon dioxide by hydrogen under pressure at higher temperatures

³⁶ *J.S.C.I.*, 1914, **33**, 984B; Badische French Pat. 468,427, Feb. 13, 1914.

³⁷ *Abhandl. Kennt. Kohle*, 1925, **7**, 78; *Chem. Abst.*, 1927, **21**, 2870.

³⁸ French Pat. 540,543, Aug. 19, 1921.

³⁹ Brit. Pat. 250,563, 1925.

⁴⁰ *Chem. Abst.*, **21**, 1927, 1128; Can. Pats. 273,983 and 273,984, Sept. 20, 1927; *Chem. Abst.*, 1927, **21**, 3908.

consist of an intimate mixture of alkali or alkaline-earth oxides with other metallic oxides. The former are obtained from the chromates, manganates, molybdates, tungstates, uranates, or vanadates of potassium, sodium, rubidium, barium, etc.; the number of atoms of alkali metal in the catalyst should amount to at least one-half, or of alkaline-earth metals one-quarter, of the total number of metallic atoms present. E.g., zinc oxide is mixed with potassium chromate, or manganese dioxide with neutral barium tungstate, the mixture made into a paste with 10 per cent of a 10–20 per cent dextrin or tragacanth solution, granulated, and dried at a temperature not higher than 320°; it is freed from dust before use. A suitable gas mixture contains about 50 volumes of hydrogen to 40 volumes of carbon monoxide. During the reduction, which is carried out at 330°–400°, the carbon dioxide and methane formed are removed by refrigeration under high pressure. The liquid reaction product separates into two layers, an upper layer (about 30 per cent) of sp. gr. 0.885–0.890 and a lower aqueous layer of sp. gr. 0.925–0.940. The alcohols in the lower layer are salted out at –20°, added to the upper layer, and the whole dried and distilled. The main fraction (about 60 per cent) consists of propyl, butyl, and amyl alcohols; hexyl, heptyl, and higher alcohols are also formed. The salt solution contains methyl and ethyl alcohols. The products may be used as a source of the corresponding saturated hydrocarbons, aldehydes, etc., or may be used directly as liquid fuels.⁴²

5442. Heating of Catalyst. Patart⁴³ secures uniform heating of the catalyst mass by rendering it conductive and passing an electric current. Thus, for the synthesis of alcohols, acids, etc., from carbon monoxide and hydrogen, the zinc oxide-chromium oxide catalyst is mixed with copper, silver, aluminum, coal, coke or graphite. Such a method would, naturally, be unavailable to control the catalyst temperature in exothermic reactions.

5443. Synthol was obtained by Fischer and Tropsch by treating carbon monoxide with hydrogen (purified water-gas) under high pressure (100–150 atmospheres) at 400°–450° C. in presence of an iron-potash catalyst.⁴⁴ The product separates into two layers, aqueous and oily. Acids (formic, acetic, propionic, iso-butyric and up to $C_8H_{16}O_2$) were found, also aldehydes (normal propyl, iso-butyl and normal butyl but not formaldehyde), alcohols and ketones (acetone, methanol, ethanol, normal propanol, methylethyl ketone, diethyl ketone, methyl normal propyl ketone), esters, and a small percentage of hydrocarbons. The result of the examination of such a product is shown in the table on page 683.⁴⁵

5444. Higher-boiling Constituents of Synthol. According to Tropsch⁴⁶ some of the higher-boiling constituents of synthol contain hydroxyl groups as is shown by the fact that they can be acetylated. Some solid paraffin and asphalt are also found.

5445. A mixture of hydrogen and oxides of carbon is passed over an iron catalyst containing alkalies and alkaline earths, at a temperature below 300° C. The products include solid oxygen-containing resins, paraffin wax, liquid containing paraffins, alcohols, and organic acids. Thus, a mixture of hydrogen and carbon monoxide is passed at 200° C. over a catalyst made by precipitating ferric nitrate with ammonia, washing and drying the precipitate, impregnating it with potassium hydroxide; and reducing with hydrogen. Copper may also be present to activate the catalyst.⁴⁷

⁴¹ French Pat. specification 598,447, 1925.

⁴² Brit. Chem. Abst., May 13, 1927, 347B; cf. Brit. Pat. 252,361, 1926.

⁴³ French Pat. 618,439, July 2, 1926.

⁴⁴ Brennstoff-Chem., 1923, 4, 276; Ber., 1923, 56, 2428; Fischer (tr. Lessing), The Conversion of Coal into Oil, 213 et seq.

⁴⁵ The greater part of the work of Fischer and Tropsch on synthol appeared for the first time on the publication of *Die Umwandlung der Kohle in Öle*, but some parts were published separately in 1923.

⁴⁶ Abhandl. Kennt. Kohle., 1925, 7, 75; Chem. Abst., 1927, 21, 2779.

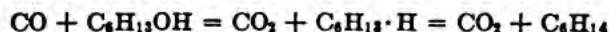
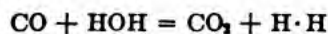
⁴⁷ Brit. Pat. 280,522, convention date, Nov. 15, 1926, to the I. G.; Chem. Age (London), 1928, 18, 57.

COMPOSITION OF SYNTHOL⁴⁸

Total Amount of Each Group	Identified	Approximate Quantity of Identified Compounds, Per Cent of Total Products
10 per cent acids.....	Formic acid.....	0.1
	Acetic acid.....	2.3
	Propionic acid.....	2.1
	Isobutyric acid.....	1.0
	Higher fatty acids up to C ₈	4.5
29 per cent water-soluble alcohols, aldehydes and ketones.....	Methyl alcohol.....	1.5
	Ethyl alcohol.....	14.5
	Propyl alcohol.....	
	Acetone.....	5.2
11 per cent oil partly miscible with water.....	Methyl ethyl ketone.....	
48 per cent oil volatile in steam.....	Propionic aldehyde.....	
	Isobutyric aldehyde.....	
	Di-ethyl ketone.....	
	Methyl- <i>n</i> -propyl ketone.....	
	Higher alcohols up to C ₈	15.0
	Esters.....	2.0
2 per cent oil not volatile in steam.....	Hydrocarbons.....	1.0

5446. Oxygenated organic compounds and acyclic hydrocarbons are obtained when oxides of carbon are passed with hydrogen over an iron catalyst containing small additions of alkalis and alkaline earths at a temperature below 300° C. and under ordinary, reduced, or slightly elevated pressure conditions. The products comprise solid oxygen-containing resins together with paraffin wax, colored oxygen-containing liquids containing paraffins, as well as alcohol and organic acids. The catalyst may be activated by the addition of such a substance as copper. According to the examples, a mixture of carbon monoxide with excess hydrogen is passed at a temperature of 200° C. over catalysts prepared (1) by precipitating ferric nitrate with ammonia, impregnating the washed and dried oxide with potassium hydroxide, and reducing the dried mixture with hydrogen, or (2) by adding caustic soda solution to an aqueous solution of ferric and cupric nitrates, and reducing the precipitate, which still contains a trace of caustic soda, with hydrogen. The products consist of a yellowish-green solid, a yellow brown oil and an aqueous solution of organic acids.⁴⁹

5447. The Badische patents of 1913 stated that the oily layer obtained by the process described consisted mainly of hydrocarbons. Fischer,⁵⁰ using excess of hydrogen, obtained an oily layer almost devoid of hydrocarbons and consisting of higher alcohols and ketones, with smaller amounts of aldehydes and acids. He remarks (*loc. cit.*) that it might well have been expected that, using excess hydrogen, the product would consist, not largely, but almost exclusively of hydrocarbons. The astonishment was therefore great, and the manner of interpretation of the observed results will be of interest. At 400° C. in the presence of the iron-alkali catalyst, excess carbon monoxide as present in the Badische process is claimed to have the same deoxygenating action on alcohols that it has upon water (the water-gas equilibrium).



⁴⁸ Fischer, *loc. cit.*, 246.

⁴⁹ I. G. Farbenind. A.-G., Brit. Pat. 280,522, convention date, Nov. 15, 1926; *Ill. Off. Jour.*, Jan. 11, 1928; *Univ. Oil Prod. Co., Library Bulletin*, Feb. 13, 1928.

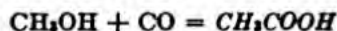
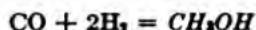
⁵⁰ *Ind. Eng. Chem.*, 1925, 17, 574.

Thus, the unexpected results are easily explained on the basis of the conditions of the experiments, excess carbon monoxide transforming the alcohols into hydrocarbons.

5448. The formation of synthol takes place best at pressures of 150 atmospheres, using as a catalyst iron filings impregnated with strong bases. The most favorable temperature is about 400°–420° C. Moreover, although the use of strong bases leads to the formation of oily products, with weak bases only water-soluble products are obtained. The relationship between these reactions and the methanol synthesis is shown by the following experiment: If a contact tube containing zinc oxide is used, and behind this but separated from it is an iron-alkali catalyst, synthol is formed. Without the iron catalyst but with all other conditions, the same, methanol only is obtained.

5449. It can therefore be concluded that the methanol formed by the zinc oxide is further changed in the presence of carbon monoxide and hydrogen and under the influence of the iron-alkali catalyst, larger molecules being formed by condensation or other reactions. This idea is confirmed by experiments reported in an article from Fischer's laboratory, which showed that methanol heated at 400° C. with an iron-alkali catalyst in a steel autoclave undergoes partial decomposition to gases and also yields oily reaction products.

5450. It is not yet clearly evident in just what way the formation of synthol takes place. A possible scheme may be set up as follows:



It is thus seen that carbon monoxide and hydrogen are used up in the same proportions in which they are present in the starting gas (1 part carbon oxide to 2 parts hydrogen.)

5451. Fischer found all of the above italicized products, partly in the aqueous layer, partly in the oily layer. The higher homologs, which are formed by the alternating action of carbon monoxide and hydrogen, are found only in the oily layer—that is, in the synthol. This synthesis apparently yields compounds with as many as 9 carbon atoms, but small quantities of solid white waxy substances have also been obtained. It is not remarkable that at 400° C. these reactions do not go beyond compounds with 9 carbon atoms, since we know from the cracking process that at this temperature the higher aliphatic compounds are unstable, breaking down to smaller molecules. In addition to the compounds specifically mentioned above, the following have been found in synthol, the principal products being alcohols and ketones:

Propyl alcohol, and higher alcohols up to C_9
 Isobutyric acid and higher acids up to C_9
 Isobutyraldehyde, and higher aldehydes
 Acetone, methylethyl ketone, diethyl ketone, methyl-*n*-propyl ketone
 About 2 per cent of various esters
 About 1 per cent of hydrocarbons

5452. As for the practical utilization of synthol, it should be stated that 87 per cent distills below 200° C., so that almost all of the crude product, after washing free from acids, can be used as light motor fuel, as practical experiments with motor vehicles have proved. Some of the physical data of synthol are therefore of interest.

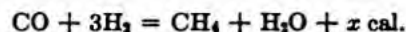
Properties of the Oil Distilled below 200° C.

Color, light yellow, not darkening on standing
 Specific gravity 20°/4° C. = 0.8289
 Carbon 69.3 per cent, hydrogen 12.3 per cent
 Higher heating value, 8200 calories per kg.
 Lower heating value, 7540 calories per kg.

Thickening point: At -30°C . separation begins, but the oil is still non-viscous. Complete solidification occurs at -90°C .

Boiling range:							
Temperature, $^{\circ}\text{C}$	62-80	100	120	140	160	180	200
Per cent	11	37	64	76	84	91	97

5453. The utilization of the heating value of the original gas mixture ($\text{1CO} + 2\text{H}_2$) is not so efficient in the case of synthol as with methanol, as Audibert has recently pointed out. The reaction



is exothermic, heat being liberated. The heat content of the 1 mol. of methane on the right-hand side of the equation is only 77 per cent of that of the 4 mol. on the left; 23 per cent of the available heat on the left-hand side has thus been lost in the formation of methane. The formation of methanol is similar, the reaction being likewise exothermic:



Eighteen per cent of the available heat is lost, the right-hand side thus having only 82 per cent of the heating value of the left-hand side. In the isopropyl alcohol formation the loss in available heat is 23 per cent; with dimethyl ketone it being about the same. Thus, although in the formation of methanol the exothermic character of the reaction causes a heat loss of 18 per cent, the loss in the formation of synthol must be about 25 per cent.

5454. Paraffins of High Molecular Weight by Synthol Process. Fischer and Tropesch (with Ter-Nedden) report that after long use in the synthol process one of the contact masses (iron-copper 4 : 1 plus potassium carbonate) was found to have accumulated a large quantity of synthesized hydrocarbons of low volatility and high molecular weight. Separation was effected partly by distillation, partly by extraction with solvents. The least soluble fraction melted at 104° – 117°C . and solidified at 109° . It was shown to consist of paraffins of the order of C_{70} .⁵¹

5455. Frolich and Lewis have studied the comparative efficiency of various catalysts in the formation of higher alcohols from carbon monoxide and hydrogen, the pressure used being 204 atmospheres. Steel or chromium-steel turnings impregnated with potassium hydroxide gave unsatisfactory results, the loss as gaseous products in most cases varying from 30 to 70 per cent. A low-chromium steel with a minimum of added alkali appeared the most effective. The highest oil yield obtained was 13.4 per cent, and increase of oil yield was associated with increase of gas losses. In combination with a methyl alcohol catalyst, gas losses were less, but only traces of oil were obtained, the product being a mixture of methyl alcohol and higher alcohols. Metallic oxide catalysts, such as a mixture of zinc oxide, chromic oxide, and barium hydroxide on copper, which yield methyl alcohol at 300° – 350° , produced higher alcohols at 450° – 500° . The best yield recorded, however, was 13.9 per cent, chiefly propyl alcohol. The loss was rather less than with iron-alkali catalysts, and the product was largely alcoholic in place of the complex mixture of alcohols, aldehydes, ketones, etc., obtained in the other case.⁵²

5456. The production of higher alcohols and other oxygenated compounds is favored, not only by modification of the catalyst but also by diminishing the rate of flow of the gases over

⁵¹ *Ber.*, 1927, **60B**, 1330; *Chem. Abst.*, 1927, **21**, 2870.

⁵² *Ind. Eng. Chem.*, 1928, **20**, 354; *Brit. Chem. Abst.* **1928**, 397B.

the contact mass.⁵³ When the mixture of carbon monoxide or dioxide and hydrogen, etc., that produces methyl alcohol if passed quickly over a contact mass is passed over a similar mass more slowly oily substances consisting chiefly of higher alcohols are produced. Special contact masses for the purpose contain alkali metals. For example, into a copper-lined vessel is charged a mass prepared by adding zinc oxide to fused potassium dichromate and subsequently reducing with hydrogen at 450°; over this is slowly passed a mixture of carbon monoxide and about 4 times its volume of hydrogen, at 200 atmospheres and 480°. The product obtained by condensation consists largely of oily matter insoluble in water. This substance is a mixture of higher alcohols together with small proportions of aldehydes, hydrocarbons, and amines (from nitrogen present in the reacting gas mixture). Other contact masses are those containing, e.g., chromium, zinc, and barium, sodium, or manganese; or tungsten, copper, and lead. The temperature at which the reaction proceeds may be from 350° to 500°, and products are obtained containing up to 80 per cent of compounds not miscible with water.⁵⁴

5456A. In the production of alcohols, acids, esters, ketones, fats and hydrocarbons from oxides of carbon and hydrogen by the use of catalysts containing elements of the 8th group, considerable quantities of carbon and methane are also formed. It is proposed to avoid the formation of these bodies by the use of catalysts of copper, silver, gold, etc., with small quantities of the iron group. Substantial amounts of iron, cobalt, or nickel may be employed with copper, silver or gold, if a pressure above 20 atmospheres is employed, and the proportion of hydrogen or methane exceeds that of carbon monoxide. The catalyst may also contain elements forming difficultly reducible oxides, such as zinc, magnesium, aluminum, chromium, etc., up to 5 per cent. The activity of the catalyst can be considerably increased by the presence of 1 per cent of alkali metal. Ferric nitrate 1 part, cupric nitrate 2 parts, and potassium carbonate 0.1 part, deposited on pumice and calcined, yield a catalyst suitable for a gas mixture containing carbon monoxide 32 per cent, hydrogen 64 per cent, and nitrogen 4 per cent, at 200 atmospheres and 350° C. Mixed nitrates of iron 12 parts, zinc 2 parts, and copper 12 parts, precipitated with potassium carbonate, give a catalyst which at 240° and 300 atmospheres converts a mixture of carbon monoxide 20 per cent, methane 8 per cent, hydrogen 70 per cent, and nitrogen 2 per cent largely into ethyl alcohol.⁵⁴

5456B. Carbon black is obtained by decomposing carbon monoxide at a temperature of 100°–450° C. and pressure of 100–200 atmospheres in the presence of iron, nickel, or cobalt, containing activating additions consisting of metal oxides such as manganous oxide, vanadium oxide, chromic oxide, uranium oxide, zinc oxide, cadmium oxide, copper oxide, or alumina, or alkalies. The carbon monoxide may be mixed with other gases to regulate the temperature.⁵⁴

5457. According to Patart⁵⁵ if a gas mixture containing, in addition to hydrogen and carbon monoxide, ethylene or its higher gaseous homologs is submitted to catalysts as in the manufacture of methanol, liquid hydrocarbons are obtained. Thus, a mixture of 23 per cent ethylene, 22 per cent carbon monoxide, 49 per cent hydrogen, 1.2 per cent carbon dioxide, 0.5 per cent oxygen, and 4 per cent nitrogen was passed over a basic zinc chromate catalyst at 300° under 150–250 atmospheres pressure; the cooled reaction product formed two layers, of which the upper (about $\frac{1}{2}$) consisted of hydrocarbons of sp. gr. 0.735, and possessed the fluorescence characteristic of some petroleum hydrocarbons. The lower layer was almost pure methyl alcohol, sp. gr. 0.805, b.p. 66°–68°. The process can be applied to gases produced by the cracking of petroleum or other oils.⁵⁴

5458. A further development of the same process⁵⁷ is described by Patart. A mixture of equal volumes of illuminating gas and water-gas is passed over a catalyst, consisting, e.g., of zinc oxide and chromium oxide, at 300° and under 150–250 atmospheres pressure.

⁵³ Brit. Pats. 227,147, Aug. 28, 1923, 229,714, Aug. 28, 1923, 238,319, May 24, 1924, all Badische Co. patents.

⁵⁴ *J.S.C.I.*, **1925**, 189B.

⁵⁵ I. G. Farbenind. A.-G., Brit. Pat. 317,808, May 18, 1928; *Chem. Age* (London), **1929**, 293; *Brit. Chem. Abst.*, **1929**, 887B; *Chem. Abst.*, **1930**, 2137. Cf. French Pat. 660,678, May 29, 1928; *Chem. Abst.*, **1930**, 130.

⁵⁶ I. G. Farbenind. A.-G., Brit. Pat. 321,402, Aug. 3, 1928; *Chem. Age* (London), **1930**, 31.

⁵⁷ French Pat. 593,648, 1925.

⁵⁸ *Brit. Chem. Abst.*, **1927**, 347B.

⁵⁹ French Pat. 594,121, 1925, to Patart.

On cooling, under the same pressure, a liquid product is formed which separates into two layers, the upper containing hydrocarbons and the lower methyl alcohol. The gaseous product is returned to the initial reaction mixture. In the last hour of the reaction the amount of methyl alcohol produced is scarcely diminished, the pressure having fallen meanwhile to only 34 atmospheres. It is better, therefore, to work at very high pressures (800–1000 atmospheres). Methane produced in the reaction is separated by refrigeration under pressure and submitted to the process of French Pat. 593,650. The residual gas mixture consists of hydrogen, nitrogen, and carbon monoxide. It is therefore possible to carry out the process without water-gas, using coal or coke-oven gas only. The liquid product may be used directly for heating or carburetting purposes, or the hydrocarbons may be separated after addition of water, and pure methyl alcohol obtained from the aqueous solution by distillation.⁵⁸

5459. Increasing Yield of Higher Alcohols. The product from the process described in paragraph 5458 is passed over the same or another catalyst, the gases and reaction chambers being heated to avoid condensation or undue temperature fluctuations. The higher alcohols are thereby produced in greater quantity than methanol.⁵⁹ The pressures used may vary from 100 to 500 atmospheres. The catalysts mentioned are mixtures of zinc and potassium oxide, copper oxide or metallic copper.

5460. Patart⁶⁰ proposes a similar process in which the added gases are ethylene, acetylene, benzene or toluene. The products are fluorescent liquid hydrocarbons, suitable as fuel for internal combustion engines, and methanol. The unsaturated hydrocarbons are mixed in the proportions of 10 to 40 per cent. Pressure should be as high and temperature as low as possible. As an example, a mixture of ethylene, carbon monoxide, and hydrogen in the proportions 1 : 1 : 2 circulates continuously over a catalyzer previously prepared in the reaction chamber by reducing basic zinc chromate with hydrogen or with the gaseous mixture and maintained at 300° C. (572° F.). The products separate in two layers, the methyl alcohol below, the fluorescent hydrocarbons above. The fresh gas mixture is introduced continuously, and any uncondensable gases formed, as methane and ethane, are continuously withdrawn.

5460A. The original idea underlying the work that led to these methods of Patart was that the addition of ethylene might lead to the formation of acetone.⁶¹

5461. Gaseous Hydrocarbons from Water-gas: High Pressure.⁶² This process, possibly, is intended for the enriching of coal-gas, using a product which has a "gas" smell, instead of the odorless water-gas. Another possibility is the production of olefines for alcohol syntheses. The conditions are: elevated temperatures and pressures, slow gas circulation. The catalysts mentioned are iron or cobalt, with either a noble metal or a difficultly reducible oxide, preferably one of Group VI.

5462. Butanol and Higher Alcohols. A good yield of butanol and higher alcohols is obtained if the carbon dioxide content of the reactant gases is kept below 3 per cent. The carbon monoxide may be replaced in part and the hydrogen wholly by ethanol and the like; hydrogen may be replaced by hydrocarbons.⁶³ The removal of the dioxide is effected continuously or periodically by solution in water or by fixation in water-containing ammonia.

5462A. A mixture of carbon dioxide, methanol and oxygen is hydrogenated under pressure by the aid of a contact mass of chromium, molybdenum or tungsten. The product is dissolved in alkali to remove a part of the unchanged methanol. The rest of the methanol is removed by adding formic acid and distilling off the methyl formate. The fraction of the distillate between 80° and 125° is 75 per cent isobutyl alcohol.⁶⁴

5463. Synthol: Deodorization and Stabilization by Further Catalytic Hydrogenation. The oxygenated compounds (synthol) obtained by the catalytic hydrogenation of carbon oxides are further treated in the vapor phase at 150°–180° C. with hydrogen and a catalyst such as nickel, cobalt, copper or platinum; aluminum hydroxide, aluminum phosphate, or oxide of thorium or of tungsten may also be present. The crude synthol may be subjected

⁵⁸ *Brit. Chem. Abst.*, 1927, 346B; cf. *Brit. Pat.* 247,932, 1925.

⁵⁹ *Brit. Chem. Abst.*, May 13, 1927, 347B. See also *Brit. Pat.* 247,177, 1925, to Patart.

⁶⁰ *Brit. Pat.* 247,178, 1925.

⁶¹ Nash, *J.S.C.I.*, 1926, 45, 876.

⁶² *Brit. Pat.* 293,573, July 13, 1927.

⁶³ *Brit. Pat.* 275,284, Mar. 4, 1926, to Johnson, an I. G. communication; *Chem. Age* (London), 1927, 17, 241.

⁶⁴ I. G. Farbenind. A.-G. (Luther and Wietzel, inventors), *Ger. Pat.* 479,829, Dec. 25, 1923; *Chem. Abst.*, 1929, 4951.

to an intermediate purification by treatment first with granular silica, then with sodium hydroxide. The final product is a colorless oil consisting of higher alcohols.⁶⁴

5464. Another method⁶⁵ is put forward for purification of synthol. The substances are treated in the hot liquid or gaseous condition, conveniently by distillation, with oxalic acid. Crystalline or anhydrous oxalic acid (2 per cent or less) is added to the liquid before distillation, or the vapor of the liquid is led over a layer of oxalic acid or of material impregnated with oxalic acid. Together with oxalic acid, porous absorption carbon may be used, or the absorption carbon may be impregnated with oxalic acid and added to the methyl alcohol or the vapor of the latter led over the mixture. The foreign odor of the synthetic methyl alcohol is thus removed. Similarly, the odor of the higher alcohols and esters is improved. Acid oxalates may also be used in place of oxalic acid.

5464A. Methyl or isobutyl alcohol obtained catalytically from hydrogen and carbon oxides are purified by use of oxidizing agents such as potassium permanganate, hydrogen peroxide, persulfates, percarbonates or hypohalites, followed by distillation.^{65a}

5464B. Separation of alcohols such as isobutyl alcohol from the crude product is effected by distilling to remove most of the methanol and treating the residue with a salting-out solution.^{65b}

5465. Hydrocarbons Direct from Synthol. If synthol is heated alone in an autoclave to 400° C. (at which temperature under atmospheric pressure it cracks) it is transformed in one hour into a petroleum-like liquid, with the simultaneous formation of water and gases. Half of the residual oil is soluble in concentrated sulphuric acid. The saturated hydrocarbons give a carbon : hydrogen ratio of 1 : 2, the fraction boiling over 150° C. has a ratio of 1 : 1.8 to 1 : 1.6. This indicates the presence of naphthenes, which is of interest since naphthenes might thus be formed from water-gas of volcanic origin.⁶⁶

5465A. It has been shown that treatment of lactic acid with water and calcium hydroxide at 360° under a pressure of 130 atmospheres yields an oil that differs from the synthol of Fischer mainly in its smaller alcohol content. Treatment of the oil with sulphuric acid affords hydrocarbons identical with the corresponding synthin fractions.^{66a}

5466. Decomposition of Synthol at Atmospheric Pressure.⁶⁷ "Synthol" (5.8 g.) on heating to 400°–480° at atmospheric pressure yielded 3.9 g. of carbon, 0.3 g. of carbon dioxide, 0.7 g. of carbon monoxide, 0.5 g. of hydrogen, 0.2 g. of methane, and 0.1 g. of hydrocarbons, these products being different from those obtained by heating it under pressure in autoclaves.

5467. Synthol Production at Atmospheric Pressure. Production of oxygen-containing organic compounds from carbon monoxide and hydrogen at atmos-

⁶⁴ Brit. Pat. 278,777, June 10, 1926, to the I. G.; U. S. Pat. 1,684,640, Sept. 18, 1928, to Schmidt, Seydel and Feller, assigned to the I. G. See also Ger. Pat. 492,245, June 19, 1925, to I. G. (Schmidt and Seydel, inventors); *Chem. Abst.*, **1930**, 2468. Similarly oxygenated organic compounds are improved in color and smell by treatment in the liquid state with hydrogen at a temperature sufficiently low to avoid decomposition and in the presence of a hydrogenating catalyst. The products to be treated may be preliminarily distilled and treated with an adsorbent. I. G. Farbenind. A.-G., Pungs, inventor, Ger. Pat. 489,280, Jan. 29, 1924; *Chem. Abst.*, **1930**, 2137.

⁶⁵ Ger. Pat. 430,623, Jan. 15, 1924, assigned to the I. G., by Müller-Cunradi; *Brit. Chem. Abst.*, **1926**, 901B.

^{65a} I. G. Farbenind. A.-G., Brit. Pat. 311,468; Feb. 16, 1928; *Chem. Abst.*, **1930**, 861.

^{65b} Davis and Imperial Chem. Industries, Ltd., Brit. Pat. 310,623, March 21, 1928; *Chem. Abst.*, **1930**, 626.

⁶⁶ Fischer, *Ind. Eng. Chem.*, 1925, **17**, 574.

^{66a} Petrov, *Ber.*, 1930, **63B**, 75–84; *Brit. Chem. Abst.*, **1930**, 322A.

⁶⁷ Tropsch, *Abhandl. Kennt. Kohle*, 1925, **7**, 49; *Chem. Zentr.*, 1926, **I**, 3583; *Brit. Chem. Abst.*, **1926**, 652B.

spheric pressure is described by Dreyfus. The products are methanol, formaldehyde, ketene, acetic acid, acetone, etc. The gases are heated in presence of catalysts which do not catalyze the formation of methane.⁶⁸ The gases may [must?] be free from organic sulphur compounds and from volatile iron compounds. The catalysts to be used are the same as those already employed for the same syntheses under high pressure.

5467A. Catalytic hydrogenation of oxides of carbon is effected at ordinary or slightly raised pressure and at temperatures ranging from about 100 to 250° by use of catalysts comprising copper and one or more oxides of a metal of groups 2 to 7, obtained by precipitating aqueous solutions of the metal salts with alkalis at moderate temperatures (usually below 30°) and reducing the washed precipitate with hydrogen, carbon monoxide or their mixtures with inert gas.^{68a}

5467B. The vapors of lower alcohols are passed at atmospheric pressure and temperature below 350° C. over a catalyst consisting of a mixture of a hydrogenating or dehydrogenating component with a dehydrating component, to obtain higher alcohols and the corresponding aldehydes and ketones.^{68b} The catalysts may be silver, copper, cobalt, iron or nickel, mixed with oxide of aluminum, thorium, iron, chromium, tungsten, titanium or beryllium. Butyl alcohol may be produced from ethyl alcohol, 2-methyl-pentanol-1 from propyl alcohol, methyl-isobutyl-carbinol from isopropyl alcohol, and methyl-propyl carbinol with methyl-isobutyl-carbinol from a mixture of ethyl alcohol and isopropyl alcohol.

5468. Synthol is prepared without external hydrogen⁶⁹ by passing a vaporized aliphatic alcohol mixed with carbon monoxide at elevated temperatures and pressures over a catalyst containing hydrogenating constituents such as copper, silver, gold, tin, lead, or the like, and hydrating constituents such as an oxide of titanium, zirconium, thorium, vanadium, manganese, etc. Products containing mixtures of higher alcohols, aldehydes, and esters are obtained. It is of advantage to add an alkali or alkaline-earth metal compound to the catalyst, and if ammonia be added to the carbon monoxide, compounds containing nitrogen are also produced. The molecular weights and boiling-points of the products vary with the time of contact, with the catalyst, and with the temperature. For example, a mixture of methyl alcohol and carbon monoxide is passed at 420° and 200 atmospheres over a catalyst containing an alkali, chromium, and molybdenum, when a mixture of higher alcohols, aldehydes, and esters derived from valeric and butyric acids and the like is obtained. Ethyl alcohol passed with carbon monoxide free from iron carbonyl at 400° and 200 atmospheres over a catalyst consisting of zinc oxide, chromium and manganese oxides contained in a tube lined with copper yields products which boil for the most part between 100° and 250°. ⁷⁰

5469. Preparation of Alcohols, etc.⁷¹ Water is treated between 15° C. and 550° C. with carbon monoxide to obtain alcohols, aldehydes, ketones, acids, ethers, esters, etc. A catalyst is used containing one of the series: potassium, sodium, magnesium, vanadium, chromium, molybdenum, manganese, iron, copper, zinc, cadmium, mercury, lead, arsenic, or antimony; with one of the series: beryllium, magnesium, aluminum, silicon, calcium, etc. Examples are given of the production of alcohols using manganese carbonate, magnesia and alumina; of formic acid using thoria and potassium carbonate; of ethers using copper, thorium and bismuth compounds; of alcohols using manganese oxide, magnesia and alumina.⁷²

5470. Carbon Monoxide Reduction—Brutzkus Process.⁷³ Water-gas, alone or mixed with hydrogen, is compressed in an apparatus resembling a Diesel engine, which may [sic] contain a catalyst, and during the compression stroke the gas is cooled and the concentration

⁶⁸ Brit. Pat. 263,503, July 1, 1925; *Chem. Age* (London), Feb. 5, 1927, 142; *Brit. Chem. Abst.*, 1927, 237B.

^{68a} I. G. Farbenind. A.-G., Brit. Pat. 308,181, Sept. 19, 1927; *Chem. Abst.*, 1930, 130.

^{68b} Neumann, Brit. Pat. 326,812, Sept. 18, 1928; *Chem. Age* (London), 1930, 493; *Brit. Chem. Abst.*, 1930, 548B.

⁶⁹ U. S. Pat. 1,562,480, Nov. 24, 1925, to G. and R. Wietzel, assignors to the Badische Co.

⁷⁰ *Brit. Chem. Abst.*, 1926, 512B.

⁷¹ Brit. Pat. application 296,049, convention date, Aug. 24, 1927, by Soc. chim. de la Grande Paroisse, Azote et Produits chimiques.

⁷² *Chem. Age* (London), 1928, 19, 419. See also French Pat. 651,167.

⁷³ The Brutzkus process is described in British Pat. 252,786 of Mar. 5, 1925.

of the gas increased by pumping in more of it. The products are cooled and liquefied and the residual gases returned to the compressor.⁷⁴ Presumably, the nature of the product depends on the catalyst.

5471. Recovery of Oily By-products. In the methanol and similar syntheses oily by-products are obtained. These may be recovered by passing the gases upwards through a digester packed with pine wood, while liquid from the same process is passed downward through the material.⁷⁵

5472. German Pat. 441,272, Sept. 26, 1924, to Wietzel and Köhler, assigned to the I. G., covers the obtaining of higher aliphatic acids ($C_8H_{16}O_2$ to $C_{18}H_{36}O_2$) from the oily products of the catalytic reduction of carbon oxides.

5472A. Crude methyl alcohol from the hydrogenation of carbon oxides is shaken with brine and a solvent (benzene) which is immiscible with the solution of the alcohol in brine.⁷⁶ On removal of the solvent and distillation of the brine, methyl alcohol is obtained free from unsaturated compounds and unpleasant odor.

5473. Utilization of Heat Evolved.⁷⁶ The utilization of the heat from exothermic carbon monoxide hydrogenations is effected by arranging the catalyst tubes in a high-pressure boiler, by equipping the reaction chamber with steam generating tubes or by placing both the steam tubes and the catalyst tubes in a bath of molten metal. In addition to the heat economy secured, secondary reactions are in this way prevented.⁷⁷

5473A. In the production of methyl alcohol from hydrogen and carbon monoxide, the heat of the reaction mixture coming from the catalyst chamber is used for the distillation and rectification of the crude liquid product obtained by the process.^{77a}

5473B. The catalyst chamber for the pretreatment of gases for the reduction of carbon monoxide surrounds the main reaction chamber so that the purifying process is facilitated by the heat generated in the main reaction.^{77b}

5474. Use of Products of Carbon Oxides Hydrogenation. The use of these oily products or, better, the products of their acylation, hydrogenation or condensation, as solvents of cellulose compounds is claimed in British Pat. 282,172, June 10, 1926, to the I. G.⁷⁸

5475. Detergents for Textiles.⁷⁹ Sodium isopropyl-naphthalene- β -sulphonate (3 parts) in water (7 parts) is mixed with a "synthol" fraction (3 parts) of b.p. 145°–165° (isobutyl and higher alcohols); or an aqueous solution of a syntan (e.g., formaldehyde-cresolsulphonic acid) is mixed with cyclohexanol. The claims cover mixtures of aromatic (excluding hydro-aromatic) sulphonic acids, having more than 10 carbon atoms in the molecule, with higher aliphatic alcohols, including alicyclic alcohols when the sulphonic acid has tanning properties.⁸⁰

5476. The oily products obtained by hydrogenation of oxides of carbon and consisting chiefly of higher aliphatic alcohols are used as one constituent of a cleansing or emulsifying agent. The other components are soap and a lower aliphatic alcohol with or without a hydro-carbon.⁸¹

5477. Brit. Pat. 282,617, June 10, 1926, to Johnson (from the I. G.), deals with use as rubber solvents of the oily products of the synthol and related processes.

⁷⁴ Brit. Chem. Abst., 1926, 954B.

⁷⁵ Brit. Pat. 249,519, 1925, to Patart; Chem. Abst., 1927, 21, 973.

^{76a} Ward and Imperial Chem. Industries, Ltd., Brit. Pat. 309,708, March 21, 1928; Brit. Chem. Abst., 1929, 845B.

^{76b} Brit. Pat. 279,347, May 30, 1927, to Johnson, an I. G. communication.

⁷⁷ Chem. Age (London), 1927, 17, 495.

^{77a} "S.I.R.I." (Soc. Italiana Recherche Industriali), French Pat. 660,108, Sept. 8, 1928; Chem. Abst., 1930, 127.

^{77b} L'Air Liquide Soc. Anon. pour L'Etude et L'Exploit. des Proc. G. Claude, Assnecs. of Soc. Chim. de la Grande Paroisse, Azote & Prod. Chim., Brit. Pat. 307,039, June 6, 1928; Brit. Chem. Abst., 1929, 978B.

⁷⁸ Brit. Chem. Abst., 1928, 155B.

⁷⁹ Brit. Pat. 244,104, Dec. 3, 1925 (convention date, Dec. 5, 1824), to Badische Co.

⁸⁰ Brit. Chem. Abst., 1927, 295B.

⁸¹ Brit. Pat. 260,243 and additional Brit. Pat. 283,786, Oct. 13, 1926; Brit. Chem. Abst., Mar. 30, 1928.

5478. The oily liquids obtained by the reduction of carbon oxides⁸² can be condensed with formation of products utilizable as motor fuels, artificial resins and solvents. Certain fractions (Brit. Pat. 238,319) condensed with hydrochloric acid yield turpentine-like liquids and with zinc chloride a solvent for nitrocellulose and also a resin.

5479. Road Test of Synthol. Road tests have been made with a 4-h.p. motorcycle whose carburetor was adjusted for benzol. Benzol gave 2.9 km. per 100 cc., synthol 3 km., benzol-synthol mixture 1 : 1, 3.2 km., benzol-alcohol-synthol 1 : 1 : 1, 2.9 km. With synthol alone there was knocking, but this was eliminated by the addition of benzol.⁸³

⁸² Brit. Pats. 227,147, 229,714, 237,030.

⁸³ Davin, *Mat. grasses*, 1925, **17**, 7267; *Chem. Abst.*, 1925, **19**, 3155.

CHAPTER LV

REDUCTION OF CARBON OXIDES

IV. SYNTHIN

5500. As we have seen, Sabatier and Senderens ¹ showed that the catalytic reduction of carbon monoxide at atmospheric pressure over a nickel catalyst resulted in the formation of methane. Until 1926 the only methods known for the production of higher homologs of methane and of methanol by reduction of carbon monoxide called for high pressures.

5501. In 1926 Fischer and Tropsch ² announced that, by using as catalysts metals of the eighth group, they had succeeded in hydrogenating carbon monoxide with the production not only of methane but also of its homologs. The catalyst first used by Fischer and Tropsch was an iron-zinc oxide mixture: this gave the gaseous homologs. Other catalysts, for instance, a mixture of cobalt and chromium oxide, caused the formation of liquid and solid hydrocarbons. The most active single catalyst they tried was finely divided metallic cobalt, next iron, then nickel.

5502. However, much better results were secured by the use of mixed catalysts—a metal of the eighth group with an oxide. The oxides tested were those of chromium, zinc, beryllium, rare earths, uranium, silicon, aluminum, magnesium, and manganese. Activated carbon and other forms of amorphous carbon were also tried. Combinations with palladium, copper and iron oxide (the latter with nickel and copper) appear to have advantages. A small amount of alkali enhances the catalytic activity. The best proportions of metal to oxide were found to lie between 1 : 1 and 1 : 3. No novel or essential method of preparing the catalysts is reported.

5503. The gases used in the earliest experiments were pure hydrogen and pure carbon monoxide, mixed in predetermined proportions. Later, water-gas was employed, rendered utilizable by a special method of purification to remove sulphur. The proportions were, generally, equal volumes of carbon monoxide and

¹ *Compt. rend.*, 1902, **134**, 514. Sabatier, *Catalysis* (tr. Reid), para. 493, *et seq.*

² *Brennstoff-Chem.*, 1926, **7**, 97 (a translation by Cutter appeared in *Nat. Petroleum News*, Oct. 13, 1926 and Oct. 20, 1926); *Ber.*, 1926, **59B**, 830–836; *ibid.*, 1926, 923. A liquid similar to benzine is claimed by Falk-Hultgren and Vidstrand to be prepared by heating a mixture of carbon monoxide and dioxide with hydrogen to at least 200° C. (Danish Pat. 18,827, July 11, 1913, *Chem. Ztg. Rep.*, **1915**, 142.) The products of dry distillation of peat, coal, etc., heated with hydrogen, afford a mixture of hydrocarbons ranging in composition between the methane and acetylene series. (Norwegian Pat. 24,576, Jan. 18, 1913.)

of hydrogen. Mixtures in other proportions were also made and tried: all, when the gas was free from sulphur, gave more or less gasoline.

5504. The temperature range was between 160° C. and 300° C. Nickel must be used, if at all, at the lowest temperatures, because it is an active catalyst for the formation of methane. At 160° C. nickel, with a supporter (apparently the reference is to one of the oxides enumerated) is still capable of catalyzing the synthin reaction. Iron can stand operation at 300° C. With a cobalt catalyst, 270° C. is a satisfactory working temperature. If with any of these catalysts the synthesis is attempted at higher temperatures than those indicated for each case, methane is the product. Indeed, if pentane be passed over the catalyst at a temperature higher than the synthin range, the pentane is replaced in the issuant gas by methane.

5505. Increased rapidity of gas flow causes an absolute reduction in methane formation: it also, naturally, reduces the yield of liquid hydrocarbons per passage. The most effective compromise will depend, one may suppose, on the possibility of utilizing the methane.

5506. Composition of Fischer's Synthin. Synthin so prepared is composed chiefly of saturated hydrocarbons, mostly gasoline fractions, with some solid and some semi-solid hydrocarbons. The percentage reacting with sulphuric acid (olefines) is small. "By our process, in addition to the hydrocarbons, only water and carbonic acid are formed. We have examined the water; it contains no acid, nor have we found any other oxygenated compound."³

5507. This statement affirming the absence of oxygenated products from synthin could not be more categorical. Nevertheless, when Elvins and Nash⁴ reported that oxygenated products (giving the iodoform reaction) were present in synthin, Fischer and Tropsch replied with a somewhat ambiguous criticism. They first criticized the technique of Elvins and Nash, yet afterwards affirmed that they had long known that synthin contained oxygenated compounds.⁵

5508. Elvins and Nash used catalysts composed of reduced oxides of manganese, cobalt and copper, impregnated with one-half of one per cent of lithium carbonate.

5509. The interest of the question of the formation of oxygenated products is largely theoretical. Fischer and Tropsch fathered a theory of intermediate unstable carbide formation. Such a carbide would have at least 1 carbon atom for each atom of bivalent metal. The carbon is transformed by the hydrogen into methylene (CH_2) which is immediately polymerized and hydrogenated with production of saturated hydrocarbons. This requires a catalyst metal capable of forming high-carbon carbides and possessed of only moderate hydrogenation activity. If the hydrogenation outstrips the polymerization ($\text{CH}_2 + \text{H}_2 = \text{CH}_4$) methane is formed. Cobalt has just the properties required: hence its high value

³ Trans. by Cutter, *loc. cit.*

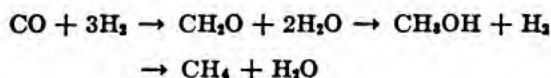
⁴ *Nature*, 1926, **118**, 154; *Chem. Abst.*, 1926, **20**, 3684.

⁵ Fischer and Tropsch. Reduction and hydrogenation of carbon monoxide. *Brennstoff-Chem.*, 1926, **7**, 299. Comment on Elvins and Nash (*loc. cit.*). Nash replied to their criticisms in: "Recent developments in the formation of synthetic fuel from carbon monoxide and hydrogen." *J.S.C.I.*, 1926, **45**, 878.

as a synthin catalyst. Now the presence of oxygenated compounds is a stumbling block in the acceptance of this view,⁶ or was so considered. Hence, probably, the reluctance of Fischer and Tropsch to admit the formation of these bodies, though that scarcely explains their categoric affirmation of such non-formation. As we have said, they have more recently⁷ admitted the formation of oxygenated compounds. This they attribute to the formation of transient oxy-carbides, which are decomposed by water vapor or hydrogen to form methanol or similar substances.⁸

5510. Elvins and Nash, commenting on the carbide theory, say that the theory of the intermediate formation of carbides advanced by Fischer does not suffice to explain the formation of oxygenated compounds. It is possible that the hydrocarbons he obtains are formed by the dehydration of alcohols followed, perhaps, by hydrogenation, but again this does not explain the absence of acids and ketones from the products obtained by him at atmospheric pressure. If the view is accepted that catalysis is an acceleration of reactions already taking place, then the formation of organic substances, other than methane and carbon dioxide, must depend on the preferential acceleration of the definite reactions which give rise to them. In the case considered here the question is complicated by the probability that not only does hydrogenation take place, but also oxidation, dehydration, and possibly polymerization.

5511. The reaction stages, if any, which lead to methane from carbon monoxide and hydrogen are possibly



and



Up to the present, however, the production of formaldehyde and methyl alcohol has not apparently been established at ordinary pressure without the intervention of extraneous sources of energy such as ultra violet light, X-rays, etc.

5512. The formation of oxygenated compounds and hydrocarbons may also be regarded as being preceded by the hypothetical formation of methyl alcohol, which is converted, according to the catalyst and the experimental conditions, into methane or into other substances. Thus the reaction may proceed in consecutive stages or the catalyst may accelerate one or more of the thermodynamically possible reactions from carbon monoxide and hydrogen. No doubt, where a mixed product of aldehydes, ketones, acids and hydrocarbons is obtained, both of these courses may be followed.⁹

5513. With regard to Fischer's intermediate oxy-carbide theory of the formation of oxygen compounds Nash remarks that it is the only one yet offered, but it lacks any experimental support.

5514. Composition of Experimental Synthin.¹⁰

(1) **Benzine.** The benzine was separated from the reaction gases from an experimental installation by absorption in activated charcoal and driving it out by steam. The raw product thus obtained was water-white and permanent to light, had a pleasant odor, and after keeping a month showed no yellowing or formation of gum. Specific gravity at 15° C. was 0.6718; calorific value 11,360

⁶ Elvins and Nash, *loc. cit.* (see next para.).

⁷ Para. 5507.

⁸ Since it is now established that "difficultly reducible" oxides are, in some cases at least, reduced in the conditions of methanol synthesis, it is conceivable that this reduction may be a factor for the formation of oxygenated compounds, in the small quantities found, in the synthin reaction.

⁹ Elvins and Nash, *Nature*, July 3, 1926.

¹⁰ From Cutter's translation, published in *Nat. Petrol. News*, Oct. 20, 1926.

calories per gram; point of spontaneous ignition in oxygen 335° C. The fractionation was carried out in an Engler flask. Amount used: 100 cc. First drop 20° C.; 40°-2.4; 50°-18.2; 60°-36.8; 70°-51.0; 80°-61.5; 90°-69.3; 100°-75.3; 110°-80.3; 120°-84.5; 130°-87.6; 140°-90.3; 150°-92.3; 160°-94.0; 170°-95.2; 180°-96.4; residue 1.6 per cent; loss 2 per cent. The following table shows the boiling-points.

Fraction Number	Boiling-point Limits	Weight, Per Cent	Specific Gravity 20-4°	C, Per Cent	H, Per Cent	C+H	C : H
I	20- 55°	26.6	0.6367	81.23	15.60	99.83	1 : 2.21
II	55- 75°	27.9	0.6488	84.48	15.46	99.94	1 : 2.18
III	75-120°	28.1	0.6838	85.04	14.98	100.02	1 : 2.10
IV	120-180°	12.0	0.7264	83.35	14.96	98.31	1 : 2.14

Fraction III had a calorific value of 11,495 cal.-gm.

Density and ultimate analysis are shown in the following table:

Fraction Number	Boiling-point Limits	Weight, Per Cent	Specific Gravity 20-4°	C, Per Cent	H, Per Cent	C+H	C : H
I	170-270°	58.4	0.7646	85.04	14.94	99.98	1 : 2.09
II	270-330°	24.1	0.7972	85.36	14.41	99.77	1 : 2.01

Fraction I had a calorific value of 11,225 cal.-gm.

(2) **Petroleum.** In the experimental plant, in addition to gas-oil and benzene, a liquid-like petroleum with the following properties was obtained. Density at 20/4° 0.7804; fractionation: 25 cc. used; first drop 170°; 180°-4.4; 190°-8.0; 200°-14.4; 210°-20.4; 220°-31.2; 230°-36.0; 240°-42.4; 250°-49.2; 260°-54.8; 270°-59.6; 280°-65.2 per cent; 290°-67.2; 300°-70.4; 310°-74.4; 320°-78.0; 330°-83.2 per cent. Residue 2.53 g. or 12.8 per cent by volume.

(3) **Paraffin.** Using an alkaline iron-copper catalyst, large amounts of paraffin wax result. The wax was separated from the adherent oil by acetone, it being noted that a portion of the oil was insoluble in the acetone.¹¹ The paraffin purified by twice crystallizing from acetone, was colorless, without odor, and had a melting point of 61° C. Elementary analysis showed: carbon 84.5 per cent, hydrogen 14.5 per cent.

5515. The catalyst is mechanically paralyzed in time by the accumulation on it of the highest members of the synthetic hydrocarbon series. These may be removed: 1. by extraction, or 2. by blowing with superheated steam, followed by reduction. It is conceivable that their deposit might be prevented by working at even lower pressures if that were practicable.

¹¹ The same is true of paraffin oils obtained from natural petroleum. The oily parts of the corresponding fractions from lignite tar are, on the other hand, soluble in acetone.

5516. Confirming the work of Fischer and Tropsch, Elvins and Nash made hydrocarbon oils at atmospheric pressure. The catalyst used was prepared from mixtures of hydrated oxides of copper, cobalt, and manganese. These were dried at 150° and then reduced in a current of pure hydrogen below 400°; the copper oxide lowers the temperature of reduction. A mixture of equal volumes of carbon monoxide and hydrogen was passed over the catalyst at a rate of 6 liters per hour with a catalyst volume of 140 cc. The carbon dioxide in the escaping gases rose from 4.3 per cent at 245° to 10.7 per cent at 284°. The gases after cooling were passed through active charcoal which by subsequent treatment and distillation yielded an oil stable to light, of composition carbon 84.1 per cent, hydrogen 14.1 per cent, and boiling range 45°–105°. ¹²

5517. In 1927 Nash and Elvins followed up this work by taking out a patent ¹³ for making olefines. The catalyst and the conditions are those mentioned in the preceding paragraph. The gas mixture to be used may be one of the commercial mixtures, such as water-gas; good yields of olefines are obtained with carbon monoxide in excess. The products are principally olefines, gaseous, liquid and solid: there are some saturated hydrocarbons and small quantities of oxygenated compounds. With equimolecular proportions of the gases, or with hydrogen in excess, paraffins are the chief product. The same result is obtained, also, if the temperature substantially exceeds 300° C.

5518. Unsaturated Hydrocarbons from Carbon Monoxide. Equal volumes of carbon monoxide and hydrogen, with a trace of oxygen, over nickel-palladium catalyst at 100° C., produced 1–3 per cent of ethylene. Other catalysts in order of decreasing activity were: nickel-copper-palladium, iron-nickel-palladium, nickel-platinum, copper-cobalt-iron, copper-palladium, copper-cobalt-nickel, carbon-palladium, nickel-copper, copper-cobalt. Nickel and nickel-palladium at 250° C. yielded 20–25 per cent of methane. ¹⁴

5519. In *National Petroleum News*, 1926, **18**, Nos. 47, 49, Fischer summarized the progress up to 1926 in the synthesis of hydrocarbons by hydrogenation of carbon monoxide, without adding materially to the information contained in the articles already cited.

5520. An important paper on experimental low-pressure synthin formation was also published at the end of 1927, by Elvins. ¹⁵ Elvins sums up as follows:

(1) Olefines may be obtained by conversion of water-gas. From these may be obtained compounds containing oxygen.

(2) It is preferable to use fairly large granules of catalyst to obviate clogging of the contact tube, due to the formation of solid hydrocarbons.

(3) Catalysts prepared by precipitation shrink on reduction, with consequent loss of activity.

(4) Fused oxide catalysts may be used, which fact effects a great saving in time of preparation over other methods and also gives a hard, stable granule.

(5) The oxygen of carbon monoxide may be eliminated almost entirely as carbon dioxide when hydrocarbons are formed.

5521. Reaction Gases. Elvins used pure gases. The carbon monoxide, stored in iron cylinders, was found to have formed some iron carbonyl as evidenced by the deposit of ferrous sulphate in the sulphuric acid scrubber and of a brown pre-

¹² *Fuel*, 1926, **5**, 263.

¹³ Brit. Pat. 291,867, Mar. 9, 1927.

¹⁴ Hoover, Dorcas, Langley and Mickelson, *J. Am. Chem. Soc.*, 1927, **49**, 873; *Chem. Abst.*, 1927, **21**, 1444.

¹⁵ *J.S.C.I.*, 1927, **46**, 473T.

precipitate in the strong potassium hydroxide with which the gas was washed. Therefore, after treatment with alkaline pyrogallate the gases were passed through a U-tube packed with activated charcoal. The charcoal removed traces of oil and of iron carbonyl.

5522. *Choice of Catalyst.* Medsforth¹⁶ had shown the effect of using promoters with dehydrating properties in conjunction with nickel, and the idea was conceived that a catalyst composed of metals and oxides with dehydrogenating and hydrogenating properties only would induce the formation of higher alcohols if not of formaldehyde and methyl alcohol. Manganous oxide was shown by Sabatier and Mailhe¹⁷ to be exclusively dehydrogenating towards alcohols and thus appeared to be suitable for the end in view as a promoter and carrier for the more important metals used as catalysts. Of the metals of the iron group, cobalt was chosen as being easier to reduce than iron, and copper was used to lower the temperature of reduction of the cobalt; accordingly copper, cobalt, and manganese oxides were used for the first experiments. Fischer and Tropesch state that the most favorable proportions of metal to oxide addition were between 1 : 1 and 3 : 1, an excess of oxide reducing the activity of the catalyst, and mixtures between these limits were accordingly prepared.

5523. The catalysts first tried were made by precipitation, advantage being taken of work on the precipitation of the oxides in an active form already published by Lamb, Bray and Frazer,¹⁸ Whitesell and Frazer,¹⁹ and Almquist and Bray.²⁰ The oxides used were those of copper, cobalt and manganese. The exact method of preparation is given in the original paper to which, because the catalysts so prepared were not found as utilisable as those made by fusion we refer any reader interested in the matter. The precipitated, washed, dried and granulated catalytic material contained 60 parts cobaltic oxide, 30 parts cupric oxide, 45 parts manganese dioxide.

5524. The dried mass was broken up and 84 cc. of granules passing 5-mesh and retained by a 10-mesh sieve were placed in the hard glass reaction tube, two plugs of glass wool being inserted to keep the mass in place. Reduction was then carried out with pure hydrogen passing over at about 8 liters per hour during fifteen hours at 120°, during three hours at 340°, and finally, during one and one-half hours, at 400°–410°. It was noteworthy that the volume occupied by the granules amounted to only 41 cc. after reduction. The temperature of the furnace was then dropped to 286° and a gas mixture of 33.4 per cent of carbon monoxide and 65.5 per cent of hydrogen was passed through the reaction tube at 9.3 liters per hour. After passing 328 liters of gas there was a contraction of volume of only 2 per cent. This represented a conversion too small for accurate measurement and the experiment was abandoned.

5525. On addition of 0.5 per cent of Li_2CO_3 to this catalyst a different result was obtained. The temperature was kept at 300° C. and the composition of the gas mixture was hydrogen 44.6 per cent, carbon monoxide 53.9 per cent. Of this 1230 liters were treated. Two charcoal U-tubes used to absorb liquid products gained in weight 7.8 g. These were steamed out at 160° C. and yielded an oily layer. Of the insoluble oil 1.4 g. was obtained and distilled between 75° and 200°. A small quantity of yellow solid organic material had collected on the cool part of the catalyst tube.

As the aqueous layer from the steam distillation had a distinct odor and an acid reaction, it was investigated for soluble organic compounds. It was neutralized with 0.33 g. of caustic potash in 0.1 *N*-solution, and the neutral solution on fractionation yielded a fraction boiling below 100°, which had a pleasant odor and formed iodoform without warming. A catalyst of similar composition to the above but without the addition of alkali also yielded an insoluble oil and a water-soluble fraction. It was noted that all the catalysts made from precipitated oxides diminished to about half-bulk on reduction, and consequently it was inferred that a considerable loss in activity must result from this, so other methods of preparing catalysts were considered.

5526. *Preparation of Catalysts by Ignition of Nitrates.* 211 g. of cobalt nitrate, 90 g. of copper nitrate, and 102 g. of manganese nitrate were melted in their water of crystallisation and

¹⁶ *J. Chem. Soc.*, 1923, **123**, 1452.

¹⁷ *Ann. Chim. Phys.*, 1910, viii, **20**, 289.

¹⁸ *Ind. Eng. Chem.*, 1920, **12**, 213.

¹⁹ *J. Am. Chem. Soc.*, 1923, **45**, 2841.

²⁰ *Ibid.*, 2305.

dried in an oven with stirring at 110°, after which the oven temperature was raised to 150°, and maintained at this temperature until oxides of nitrogen were no longer evolved. The material obtained was powdered to pass a 30-mesh sieve and the contact tube filled so that only a narrow channel was left for the passage of the gases. Residual nitrates were decomposed by heating the tube to 300° and passing a rapid stream of nitrogen until the escaping gas did not redden litmus, after which the oxides formed (in the proportion of 60 parts Co_2O_3 , 30 parts CuO , and 45 parts MnO_2) were carefully reduced in a current of hydrogen up to 410°. At 295° a mixture of 48.2 per cent carbon monoxide and 51.2 per cent hydrogen was passed over the catalyst so obtained; after twelve minutes water rapidly formed in the cool part of the tube and 1.5 cc. formed in four and one-half hours at a gas rate of 6 liters per hour. A contraction of 60 per cent was observed and the escaping gas contained 50.8 per cent carbon dioxide, but after forty-eight hours the reaction tube clogged, so it was cooled and half of the catalyst removed, when it was noted that the oxides were pyrophoric. After reduction of the catalyst left in the tube (35 cc.), the experiment was recommenced at 290°–294° and the gas rate kept at about 5 liters per hour for some 188 hours. After three hours at 5.5 liters per hour the contraction amounted to 12 per cent, and after 141 hours to 8 per cent, and it was again noticed that at the beginning of the reaction much water formed, but this gradually diminished until no more appeared in the receiver inserted in front of the charcoal absorbers. When 1198 liters of the gas mixture mentioned had been passed over the catalyst the two charcoal U-tubes gained in weight 6.6 g., and 0.10 g. of a light yellow wax which softened at 64° and melted at 68°–69° was obtained from the end of the reaction tube, while 2.67 g. of an insoluble oil was obtained by steam-distilling the contents of the two charcoal U-tubes. Fractionation of the aqueous layer from the steam distillation gave about 20 cc. of distillate below 100°, which separated into two layers, showing the presence of oxygen-containing substances only partly miscible with water. It appeared from this experiment that reduced unsupported oxides prepared by ignition of the corresponding nitrates gave a much greater conversion than the reduced precipitated oxides.

5527. Size of Granule. It is desirable to reduce the size of granule as much as practicable, in order to increase the active surface. But when a tube was filled, in such a way as to leave no channel, with 30–60 mesh material, it clogged in forty-eight hours, owing to the cementing of the granules by high-boiling hydrocarbons.

5528. The optimum conditions for the production of olefines and solid or liquid products were found to be equal volumes of carbon monoxide and hydrogen and a working temperature of about 300° C.

5529. The original article should be consulted for details of a number of experiments with different gas proportions and at various temperatures, as also for analyses of products and effluent gases. Elvins regards the advance in the synthesis of olefines as the most important result, since from these hydrocarbons, by well-known methods, many valuable oxygenated products may be obtained. Commenting on the utilization of methane, ethane and propane as potential sources of ethylene and acetylene, Nash²⁰ observes that the polymerization of ethylene to light spirits or heavier oils is of fundamental interest, and may ultimately be shown to constitute a source of synthetic lubricant hydrocarbons. Ethylene and acetylene, he adds, may also be looked upon as possible sources of alcohol base fuels when such processes reach full technological development.

5530. A recent paper by Erdeley and Nash²¹ reports experiments with different catalysts: cobalt-copper-alumina, cobalt-copper-manganese oxide, cobalt-copper-zinc oxide, cobalt-copper-cerium oxide, cobalt-copper. These catalysts were prepared by ignition, followed by reduction of the oxides. The general method was similar to that followed by Elvins (*loc. cit.*).

²⁰ *J. Inst. Petroleum Tech.*, 1930, **16**, 313.

²¹ *J.S.C.I.*, 1928, **47**, 219T.

5531. The results are summarized as follows:

(1) Comparing the experiments carried out with different plain catalysts at 285° and with a gas mixture containing equal parts of carbon monoxide and hydrogen, the cobalt-copper-zinc oxide catalyst appears to be the most suitable. After the initial period its activity was fairly constant, causing a contraction of about 50 per cent for several days. Nearly as constant as this was the cobalt-copper-alumina catalyst but less oil and more water was formed in its presence. The oil yield was the highest with the non-promoted cobalt-copper catalyst, the activity of which, however, decreased most rapidly. The cobalt-copper-ceria catalyst produced the smallest yield of water and a fairly good yield of oil, but although the contraction in the initial period was the highest in the presence of this catalyst, its activity decreased nearly as rapidly as that of the non-promoted catalyst.

(2) Catalysts supported on silica gel were only as active as the plain catalyst in one case (manganese oxide-cobalt-copper). The importance of the relative proportions of silica gel to the catalyst substance was investigated as certain mixtures were found to have greater activity than others.

(3) The best temperature for the formation of liquid hydrocarbons was found in the case of cobalt-copper-alumina to lie between 280° and 290°. Above this, chiefly carbon dioxide and methane were formed. Below 230° no reaction could be observed.

(4) An excess of hydrogen in the original gas mixture increased the formation of water, while an excess of carbon monoxide lowered the activity of the catalyst very quickly.

(5) The gas velocity was shown to exert a great influence on the yield of products. The optimum space velocity was found in the case of cobalt-copper-zinc oxide catalyst to be about 120 volumes of gas per hour per unit volume of catalyst.

5532. An investigation of the formation of hydrocarbons from water-gas, which was marked by exceptional care and precision, was carried out at the Pittsburgh station of the U. S. Bureau of Mines by Smith, Hawk and Reynolds.²² All the catalysts were made as follows: (1) 881 g. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 150 g. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 183 g. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 3 liters of water and the solution filtered; (2) 220 g. NaOH dissolved in 500 cc. water were added slowly with stirring to the solution (1) heated to 85° C.; (3) the precipitate was washed by decantation until it began to become colloidal; (4) it was then filtered on muslin, compressed into pellets about 8 mm. long and 2 mm. in diameter, and dried slowly up to a final temperature of 200° C.; (5) the dried catalyst, freed from fines, was placed in the catalyst tube and reduced, first at 150° C., with hydrogen diluted with nine times its volume of nitrogen, the temperature and hydrogen concentration being increased, finishing with pure hydrogen at 300° to 325° C.

5533. The water-gas used was freed from oxygen, hydrogen sulphide, carbon dioxide, and water vapor, and finally from all sulphur compounds and heavy gases through a trap cooled in liquid air. Purification from the last trace of sulphur is a prime necessity.

5534. A mixture of the fused nitrates of sodium, potassium, and lithium was used as the heating liquid in the thermostat containing the reaction tube in which the catalyst was placed. Since the reactions evolve considerable quantities of heat, the thermostat temperatures only approximate to those of the catalyst mass. The reaction tube was designed to reduce as far as possible this probable difference in temperature. Experiments were made at temperatures between 203° and 287° at space velocities from 120 to 260. At 203° 18 per cent of the gas is converted in a single passage at a space velocity of 230. It was noticed that the activity of the catalyst fell very rapidly (as judged by the amount of gas converted) as the volume of gas

²² *Ind. Eng. Chem.*, 1928, **20**, 1341.

passed over increased, to reach a fairly steady value. Passage of hydrogen over the catalyst reactivated it. Most of the oxygen appears in the product as water, and the ratio $H_2O : CO_2$ increases rapidly with decreasing temperature. At the higher space velocities and at the higher temperatures relatively more unsaturated hydrocarbons are formed; with lower velocities and at the higher temperatures, in general, more heavy hydrocarbons are formed. The total hydrocarbon products contain, according to conditions, from 20 per cent by weight upwards of methane. In one experiment at 260° with a space velocity of 260 the composition of the hydrocarbon products was: methane 21 per cent, "gasol" 45 per cent, motor fuel 34 per cent. The yields of hydrocarbons other than methane vary from 92 to 156 g./m.³ of hydrogen and carbon monoxide converted. Some degree of control can be exercised over the nature of the product by suitable choice of the variable conditions.²³

In the practical operation on a large scale, the catalyst chamber would have to be designed to carry away efficiently the heat of the reaction and to maintain rather close temperature control throughout the large catalyst mass.

5535. In another article Fischer and his co-workers report that the "gasol," benzine, and petroleum fractions of the synthetic petroleum obtained by the catalytic reduction of carbon monoxide at ordinary pressures have been examined. The "gasol" consists of ethane, propane, and butane, together with the corresponding olefines; after twenty-four hours' operation an iron-copper catalyst gave a product containing 26.5 per cent of olefines, while after sixty-five hours the proportion rose to 36 per cent. The benzine (initial b.p. 59°), of which 95 per cent distilled below 185° , had d_{40}^{20} 0.7135, iodine value 161, and contained 65 per cent of *unsaturated* hydrocarbons. The latter are probably simple olefines, the benzine being stable to light and air and showing no tendency to discolor or deposit gums. By varying the experimental conditions it is possible to obtain more highly saturated benzines if desired. *n*-Octane, *n*-nonane, and isononane were identified in the saturated hydrocarbons remaining after exhaustive extraction with fuming sulphuric acid of a fraction of boiling range 125° – 150° . The iodine value of the petroleum fraction varied considerably with the experimental conditions, e.g., from 8.7 to 64.7. It increased with the gas velocity and with the age of the catalyst. The water-soluble organic products of the reaction amounted at most to 2 per cent of the total products, and consisted principally of aldehydes and ketones.²⁴

5535A. A benzine distillate of the synthetic petroleum obtained by the catalytic reduction of carbon monoxide under ordinary pressures has been found to consist of a mixture of olefines (65 per cent) and paraffins, containing only small amounts of aromatic hydrocarbons (benzene 0.1 per cent, toluene 0.4–0.5 per cent), and no naphthenes. The benzine was fractionated and the olefines and paraffins were separated. The following hydrocarbons were isolated and identified: $\Delta\alpha$ - and $\Delta\beta$ -pentenes, $\Delta\alpha$ - and $\Delta\beta$ -hexenes, $\gamma\gamma$ -dimethyl- $\Delta\alpha$ -pentene, heptene, (?) $\Delta\beta$ -octene, nonene, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, γ -methyloctane, *n*-nonane. A small quantity of a solid crystalline substance (m.p. 106°) of unknown constitution, but possessing some of the properties of a γ -pyrone derivative was isolated from the fractions of b.p. 100 – 120° .^{24a}

5536. Smith, Davis and Reynolds²⁵ worked on the low-pressure synthin process. The water-gas used in these experiments, undertaken for the sake of obtaining more quantitative information than was available upon the production of high hydrocarbons from water-gas at atmospheric pressure, was made from charcoal and contained about equal proportions of hydrogen and carbon monoxide. The catalysts tried included promoted iron, cobalt-copper-chromium oxide, cobalt chromate, cobalt-copper, cobalt-copper-uranium oxide, and cobalt-copper-manganese oxide. The first five gave only negligible yields of hydrocarbons. The yields with the sixth could be measured, with some difficulty. The best yields of oil were obtained at about 275° C. (527° F.). The hydrocarbons formed included both saturates and unsaturates and in a typical case 2.5 per cent of hydrocarbons above butane was found. Oil yield decreased very rapidly with increased rate of flow of the gas over the catalyst from 200 to 360 cc. per min.

5537. Calculations show that at 20 cents per 1000 cu. ft. the cost of the water-gas for making a gallon of oil would be 28 cents. Or, if all hydrocarbons from butane up were included in

²³ *Brit. Chem. Abst.*, 1929, 82B.

²⁴ Fischer and Tropsch (with Koch), *Brennstoff-Chem.*, 1928, 9, 21; *Brit. Chem. Abst.*, 1928, 324B.

^{24a} Tropsch and Koch, *Brennstoff-Chem.*, 1929, 10, 337–346; *Brit. Chem. Abst.*, 1929, 1003B.

²⁵ *Ind. Eng. Chem.*, May 1928, 462.

the oil, the cost would be cut to 22 cents; and with the value of the unused combustible gases taken into account, the figure could probably be brought down to about 15 cents per gallon.²⁶

5538. Production of Paraffin Hydrocarbons with More than One Carbon Atom. Oxides of carbon, mixed with hydrogen, are reduced to paraffins higher than methane by heating the gases at about the ordinary pressure in presence of a catalyst at temperatures between that at which the catalyst begins to act and that at which methane is the main product. The temperature employed is generally 80°–100° below that at which methane only is formed. E. g., using as catalyst a mixture of zinc oxide and finely divided iron, at 300° the product contains 10 per cent of methane and 90 per cent of higher paraffins while at 430° methane is the only hydrocarbon.²⁷

5538A. In the production of hydrocarbons and oxygen-containing compounds containing a plurality of carbon atoms, the operation is effected in a circulatory system with a gas mixture containing only the reactants in requisite proportion for the reaction and extraneous gases such as methane, ethane, nitrogen or rare gases to the extent of at least 40 per cent by volume.^{27a} It is stated that the process is especially suitable for the production of liquid hydrocarbons with catalysts containing iron and cobalt, and to the manufacture of acids, esters, alcohols, ketones, etc., by use of catalysts containing iron, cadmium and copper, or potassium, zinc and chromium, or zinc, chromium and manganese. The reaction gases are preferably freed from carbon dioxide, sulphur compounds and iron carbonyl.

5539. For the synthin process, oxides of carbon are reduced by hydrogen, or gases rich in hydrogen, in the presence of contact masses containing, in addition to metallic copper, silver, gold, or zinc, elements of the eighth periodic group, and, if desired, small quantities of other elements or compounds. The process may be carried out under ordinary or higher pressures, and at elevated temperatures, in the absence of carriers of low heat conductivity.²⁸

5540. A combination of processes leading from coal, by low-temperature carbonization, to water-gas, synthetic hydrocarbons, methanol, and, eventually, to pure hydrogen for the ammonia synthesis has been described. It seems that this combination of processes rather than any evident novelty in the individual steps constitutes the subject-matter.²⁹

5540A. Gases containing carbon oxides and hydrogen (produced by treating solid fuels, in a producer with air and steam) are treated at 80° and at about atmospheric pressure with a catalyst formed mainly of the sulphates of cerium and cobalt.^{29a} The product comprises about 90 per cent hydrocarbons and the remainder is chiefly ketones; it may be used as liquid fuel or as a solvent for fatty materials, rubber, cellulose acetate or other substances.

5541. Sulphide Catalysts.³⁰ We find sulphide catalysts proposed in the synthesis of hydrocarbons and oxygenated products by hydrogenation of carbon oxides. Such catalysts may be metallic sulphides, such as copper or cobalt sulphides, or zinc chromates or metallic oxides which have been treated with hydrogen sulphide. Pressures of 10–100 atmospheres and temperatures of 200°–600° C. are mentioned. An example is given of the production of a petroleum-like oil by passing water-gas at 20 atmospheres through an aluminum-lined chamber containing cobalt sulphide heated to 270° C.³¹

5542. Metal Catalysts from Carbonyls. The process described in para. 1357 is applied for the production of finely divided metal (iron, cobalt, nickel or molybdenum) catalysts.³² The powder is used as such or extended on active silica. Preference is, however, expressed for the flaky form produced as described in Specification 269,677 (see para. 1357). These

²⁶ *Univ. Oil Prod. Co. Bull.*

²⁷ *Brit. Chem. Abst.*, **1927**, 695B; *Brit. Pat.* 255,818, Mar. 26, 1926, to Fischer and Tropsch. *Can. Pat.* 265,063, Oct. 19, 1926.

^{27a} I. G. Farbenind. A.-G., *Brit. Pat.* 313,467, Feb. 9, 1928; *Chem. Abst.*, **1930**, 1118; *Cf. French Pat.* 664,420, Nov. 22, 1928; *Chem. Abst.*, **1930**, 860.

²⁸ *Brit. Chem. Abst.*, **1928**, 664B.; *Cf. French Pat.* 635,950, June 14, 1927; *Brit. Pat.* 293,185, June 9, 1927, to Johnson (an I. G. patent).

²⁹ *Brit. Pat.* 282,573, Feb. 22, 1927, to Synth. Ammonia & Nitrates, Ltd., and Humphrey, *Ill. Off. Jour.*, Feb. 15, 1928.

^{29a} *Compagnie Générale des Produits de Synthèse*, *Brit. Pat.* 316,945, Aug. 6, 1928; *Chem. Abst.*, **1930**, 1866.

³⁰ *Brit. Pat.* application 269,521, convention date, Apr. 14, 1926, by the I. G.

³¹ *Chem. Age* (London), 1927, **17**, 605.

³² *Brit. Pat.* application 271,452 (convention date, May 22, 1926; addition to 267,554) by the I. G.

metals, or the oxides produced from them by burning, are used in the production of hydrocarbons from carbon monoxide and hydrogen.³³

5543. In another method of using the carbonyls,³⁴ carbonyls of iron, cobalt, nickel, or molybdenum are heated in presence of hydrogen, or water-gas or steam to a temperature sufficient to decompose the carbonyl. The deposited metal is re-converted into carbonyl and hydrocarbons are extracted from the gas by active silica.³⁵

5544. General Preparation of Hydrocarbons by the Reduction of Organic Substances. Use of Carbon and of Carbon Monoxide. Campardou,³⁶ by the use of carbon monoxide in presence of wood charcoal as catalyst at 400°–450° C. obtained yields up to the theoretical of vinyl or ethylenic hydrocarbons with organic compounds containing hydrogen and oxygen, alcohols and ethers affording vinyl hydrocarbons, while acids, ketones, and aldehydes yielded olefines. The two reactions



and



thus appear general in organic chemistry. Reduction according to equation (2) is practically always exothermic and is independent of pressure, and is accordingly best conducted at the lower limit of the activity of the catalyst. Reduction according to equation (1) is often endothermic, and requires a relatively high temperature, limited by decomposition of the hydrocarbons. The conversion of phenol into benzene according to equation (1) absorbs 20 g.-cal., whereas reduction by equation (2) liberates 22.4 g.-cal.³⁷

5544A. The temperature required in the catalytic production of olefines from mixtures of hydrogen and carbon oxides is controlled by a fluid which circulates in heat-exchanging relation with the catalyst but not in contact with the reaction gases. The temperature control fluid may be passed through passages in manganese-copper shelves on which the catalyst is placed.^{37a}

5545. Action of Acetylene on Oxides of Carbon. Sandonnini³⁸ reports, in great detail, experiments on the reaction of carbon monoxide and of the dioxide and acetylene without catalysts and in the presence of various catalysts. The object was to throw light on the formation of higher hydrocarbons in the carbon oxides hydrogenation syntheses.

5546. Production of Acetylene Hydrocarbons. Acetylene and its homologs are produced by incomplete combustion of gaseous mixtures of hydrogen, methane, and carbon monoxide, in the presence of catalysts (platinum, nickel, copper, vanadium, oxide of iron, etc.).³⁹

5547. Production of Synthetic Petroleum by Andry-Bourgeois and Oliver's Process. Water-gas is produced from cheap carbonaceous material, the carbon monoxide is converted by catalytic reduction at 230° under atmospheric pressure into methane, which is then decomposed into acetylene and hydrogen in an electric furnace at 2000°, and the acetylene is converted into a mixture of gaseous and condensable hydrocarbons of the ethylene, cyclic, and naphthene series, by catalytic hydrogenation at 150°–300° under 0.5 atmosphere pressure. Peat-coke or lignite-coke containing 20 per cent of ash (1 kg.) yielded 250 g. of a brown, dichroic liquid having a strong smell of petroleum, with *d* 0.8, calorific value 2750, and containing 75 per cent of boiling-point below 150°. A considerable quantity of the liquid could be sulphonated and oxidized, and it contained aromatic hydrocarbons in quantities comparable to Borneo petroleum. Worked on a semi-industrial scale the process has yielded a synthetic fuel which gives a petroleum spirit of sp. gr. 0.76 and a heat value of 11,539 calories per kilogram.⁴⁰

³³ *Chem. Age* (London), 1927, **17**, 115.

³⁴ I. G., British application 270,705, convention date, May 10, 1926.

³⁵ *Chem. Age* (London), 1927, **17**, 64.

³⁶ *Compt. rend.*, 1927, **184**, 828.

³⁷ *Brit. Chem. Abst.*, 1927, 440B.

^{37a} I. G. Farbenind. A.-G., Brit. Pat. 310,999, Feb. 6, 1928; *Chem. Abst.*, 1930, 625.

³⁸ *Gazz. chim. ital.*, 1927, **57**, 781; *Chem. Abst.*, 1928, **22**, 758.

³⁹ Brit. Pat. application 282,690, convention date, Dec. 21, 1926, by Soc. d'Etudes et d'Exploit. mat. org.; *Chem. Age* (London), 1928, **18**, 184.

⁴⁰ Goutal, *Chal. et Ind.*, 1924, **5**, Suppl. 90; *Chem. Zentr.*, 1925, **96**, II, 114; *Brit. Chem. Abst.*, 1924, **43**, 1087B.

5548. The Synthesis of Petroleum Hydrocarbons. Fischer⁴¹ reviews the various processes. The following special points are noted: at high pressures, with alkaliized iron catalyst synthol is produced, with zinc oxide, methanol. At atmospheric pressures, with ferrous metal catalysts, hydrocarbons from butane to solid paraffin result. Of the ferrous metals cobalt is the most active. The temperature should be between 200° and 300° C. and gas ratio H₂: CO should be 1:1. Higher temperature causes the formation of methane. Strong bases in the catalyst produce solid paraffin. If water-gas is used special care must be taken to eliminate organic sulphur.

5549. Aromatic Hydrocarbons: Synthesis.⁴² Water-gas under pressure (50 atmospheres) is passed over an iron-silver catalyst at 370° C. There results a mixture of olefines and paraffins. After cooling in a heat-exchanger and washing (still under 30 atmospheres pressure) with water, the mixture is passed at atmospheric pressure through a copper tube, filled with iron-free copper turnings, at 800° C. The gas after the first operation, before washing, contains 13 per cent olefines, 10 per cent ethane, and 4 per cent methane; the washed gas, after being subjected to the second treatment, yields 80 per cent of benzol.

5550. Gessmann and Shalders⁴³ claim a method of producing low-boiling hydrocarbons by passing unsaturated hydrocarbon gases with carbon monoxide and hydrogen over a catalyst activated by chemically active light rays. No external heat is applied and the operation is conducted at atmospheric pressure. The catalyst consists of pure powdered electrolytic copper, tungsten and pumice stone powder treated with dilute solution of caustic alkali and dried quickly.

5551. According to one of Prud'homme's proposals,⁴⁴ in producing a liquid fuel generally suitable for the same uses as gasoline, he mixes water-gas or Dowson gas with a gas rich in hydrocarbons especially those of the acetylene series and the mixture is passed first over a hydrogenation catalyst, then over a dehydrogenation catalyst and finally over catalysts to effect polymerization of the acetylene hydrocarbons.⁴⁵

5551A. Synthesis of Light Hydrocarbons.⁴⁶ A mixture of carbon monoxide and hydrogen is first heated in the presence of a catalyst such as metals of the iron group (e.g., iron, nickel, cobalt, etc., in grains or powder on refractory carriers such as alumina, calcium oxide or magnesium oxide) or sulphides such as those of iron, molybdenum and tungsten, at about 500°, and the gases are then subjected to a simultaneous expansion and cooling of sudden character to a temperature of 180°–300° again in the presence of catalysts such as finely divided metals.

5551B. Mixtures of oxides of carbon and hydrogen are treated at increased pressure and temperature with catalysts consisting of metals of the eighth group, alkali metal compounds and small quantities of free or combined sulphur, selenium or tellurium.⁴⁶ Liquid products of olefinic character are obtained and may be employed in liquid fuels to prevent knocking, for the manufacture of lubricating and insulating oils by condensation by means of aluminum chloride, boron fluoride, etc., for catalytic production of benzene hydrocarbons, and for manufacture of alcohols, glycols, etc. To obtain the catalysts, alkali sulphide or hydro-sulphide is added to the metal hydroxide obtained by precipitation with ammonia. One or more of the metals of the eighth group may be used, and other substances may be added, such as copper, silver, gold or cadmium, and alkali metal chlorides. Low temperatures and high pressures tend to form high molecular by-products such as paraffins and waxes. Thus, iron and cobalt hydroxides precipitated by means of ammonia are impregnated with potassium sulphide solution, and reduced with hydrogen. With this catalyst, employing ordinary pressure and a temperature of 267° C., liquid hydrocarbons, 10 per cent of which boil above 180° C., are obtained.

⁴¹ *Brennstoff-Chem.*, 1927, 8, 1; *Chem. Abst.*, 1927, 21, 1357.

⁴² Brit. Pat. 297,179, July 13, 1927, to the I. G.

⁴³ Can. Pat. 282,392, Aug. 14, 1928.

⁴⁴ Brit. Pat. 238,931, May 23, 1924.

⁴⁵ *Chem. Abst.*, 1926, 2063.

⁴⁶ Mercier, Brit. Pat. 312,916, June 2, 1928; *Chem. Abst.*, 1930, 860.

⁴⁶ I. G. Farbenind. A.-G., Brit. Pat. 322,284, Oct. 11, 1928; *Chem. Age* (London), 1930, 102.

5551C. Liquid hydrocarbons are obtained when hydrogen or water-gas, steam, and methane, or ethane are injected into a blast-furnace and the exit gases are led over a nickel, cobalt, or platinum catalyst at 100°–450°, preferably under pressure. With a zinc oxide catalyst alcohols are obtained; with aluminum chloride, polymerized products.⁴⁵

5552. Regenerating Metal Catalysts Contaminated with Sulphur.⁴⁶ Prud'homme treats sulphur-contaminated catalysts, e.g., those used in synthesis of light hydrocarbons, with acetic, formic or other suitable organic acid to eliminate the sulphur as hydrogen sulphide.⁴⁷

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5554A. Kodama. The catalytic reduction of carbon monoxide under normal pressure. Preparation of liquid hydrocarbons by means of cobalt-copper-thoria catalysts. *J. Soc. Chem. Ind. Japan* (suppl. binding), October, 1929, 285 (in German); *Chem. Age* (London), 1929, 406.

5554B. Odell. Possibilities in synthetic hydrocarbon processes. The commercial and economic possibilities of making hydrocarbons synthetically from water-gas are discussed in some detail. *Gas Age-Record*, 1928, 63, 37–41, 48–50; *Chem. Abst.*, 1929, 4553.

5554C. Randall and Shiffler. Deposition of carbon in the reaction between carbon dioxide and hydrogen. A new equation: $\text{CO}_2(\text{g}) + 2\text{H}_2(\text{g}) = \text{C}(\text{graphitic}) + 2\text{H}_2\text{O}(\text{g})$, is offered as a possible explanation for the results presented by Randall and Gerard (*Chem. Abst.*, 1929, 814), although the mechanism may involve a series of reactions. *Ind. Eng. Chem.*, 1929, 21, 941; *Chem. Abst.*, 1930, 333. Cf. para. 5417.

V. OTHER CARBON OXIDE REDUCTIONS AND RELATED SYNTHESSES

5555. By suitable variations in the conditions of the reduction of carbon monoxide by hydrogen, other products than methanol, methane, synthol and synthin can be made.

Ketene. One of the simplest compounds so obtained is ketene, $\text{CO}:\text{CH}_2$. According to Dreyfus ⁴⁸ mixtures of 3 molecules of carbon monoxide to 1 molecule of hydrogen yield ketene when heated at about 400°–450° (preferably 200°–300°) under pressures of about 200 atmospheres (generally 50–150), in the presence of catalysts which can effect the combination of the gases to form oxygenated organic compounds. Such catalysts are zinc or copper oxide or chromate, copper, zinc, or tin with potassium or sodium carbonate or acetate, etc. The ketene may be used directly for the production of acetic acid, etc., or removed by cooling and liquefaction.

5556. Formic Acid. It is relevant to note that Arsem produces formic acid by causing water and carbon monoxide to react under pressure in the presence of a cuprous halide catalyst.⁴⁹

5557. Synthesis and Polymerization of Formaldehyde. When a mixture of equal volumes of carbon monoxide and hydrogen was passed at 150°–180° over a mixture of pumice and zinc

⁴⁵ Fohlen, French Pat. 631, 927, April 14, 1927; *Brit. Chem. Abst.*, 1930, 406B.

⁴⁶ U. S. Pat. 1,640,668, Aug. 30, 1927.

⁴⁷ *Chem. Abst.*, 1927, 21, 3431.

⁴⁸ Brit. Pat. 262,364, 1925; *Brit. Chem. Abst.*, Feb. 18, 1927, 125B.

⁴⁹ U. S. Pat. 1,606,394, 1926; *Brit. Chem. Abst.*, Feb. 18, 1927, 125B.

dust with 2 per cent of magnesium oxide and 1 per cent of lead oxide, formaldehyde was formed, together with caramel-like polymerization products. When the resultant gases were passed into lime water containing a little magnesium oxide, only polymerization products were obtained. These contained formose and α -acrose, but, contrary to the statement of K. and W. F. Short, no dextrose.⁵⁰

5557A. Catalytic Production of Aldehydes and Alcohols.^{50a} A catalyst is used containing cobalt (suitably in the form of its chromate or nitrate as prepared) together with zinc or chromium oxides, or zinc and manganese oxides (or a mixture of all these oxides). Copper also may be present or may constitute the lining of the reaction chamber. High temperatures and pressures are used.

5558. Synthetic Formaldehyde from Carbon Monoxide and Hydrogen. Mechanism of the Sensitized Photochemical Reaction. The dependence of the rate of formation of formaldehyde on the concentrations of hydrogen and carbon monoxide has been studied in the photochemical reaction sensitized by mercury. An equation of the form $d[\text{CH}_2\text{O}]/dt = K p_{\text{H}_2}^{1/2} p_{\text{CO}} (1/p_{\text{total}})^{1/2}$ has been deduced theoretically, but the results actually obtained indicate that the equation $d[\text{CH}_2\text{O}]/dt = K p_{\text{H}_2}^{1/2} p_{\text{CO}}$ determines the velocity. Atomic hydrogen is thus one of the constituents taking part in the reaction, of which formaldehyde is the chief product.⁵¹

5559. Considerable amounts of free formic acid are obtained by the action of hydrogen and palladium-black under pressure on carbon dioxide in presence of water, while formic acid is decomposed catalytically into carbon dioxide and hydrogen. The determination of the equilibrium between these reactions between 30° and 90° C. gave no indication of the formation of formaldehyde as an intermediate product, so that it is unlikely that the formation of formaldehyde is a stage in the assimilation of carbonic acid in nature.⁵²

5560. Methyl Ether from Carbon Monoxide. A mixture of carbon monoxide 2 parts and hydrogen 1 part at a pressure of 150 atmospheres is passed through a chamber lined with inert material and containing a hydrogenation catalyst and a dehydration catalyst. The part containing the hydrogenation catalyst only is heated to 500° C. and the construction is such that the temperature at the dehydration is 300° C. while the pressure at the outlet is 25 atmospheres. A solution of methyl ether in water collects in a high-pressure condenser and tank system.

5561. The hydrogenation catalyst must be one that does not favor the formation of methane, e.g., zinc oxide and reduced chromium or copper salts. The dehydration catalyst may be partially dehydrated aluminum or titanium hydroxide, thorium hydroxide or silica gel. The process is essentially a dehydration of methanol: in fact an alternative method proposed consists in the treatment of methanol with the dehydration catalyst only.⁵³

5561A. Dimethyl Ether.^{53a} A copper-chromium oxide catalyst in contact with a 2 : 1 hydrogen-carbon monoxide mixture has been found to yield, in addition to methanol, large quantities of dimethyl ether. The catalyst contained copper and chromium in the mol ratio 3 : 1 and was precipitated from the nitrates with sodium hydroxide. The conversions of carbon monoxide at 180 atmospheres, expressed in mol per cent, to methanol and to methyl ether were, respectively: at 265° C., 7 and 4; at 285° C., 14 and 6; at 305° C., 24 and 22; at 340° C., 17 and 20; and at 355° C., 11.5 and 13.5. The region of maximum conversion was 315° to 320° C., and the conversions were of the order of 30 mol per cent, that to ether being the larger.

5562. Acetic Acid. Dreyfus, by modification of the gas mixture and catalysts, obtains acetic acid. Approximately equimolar mixtures of hydrogen and carbon monoxide yield acetic acid when heated below 350°–450° (preferably 200°–300°), at pressures up to about

⁵⁰ Vogel, *Helv. Chim. Acta*, 1928, **11**, 370.

^{50a} Morgan and Taylor, Brit. Pat. 313,061, Feb. 28, 1928; *Chem. Abst.*, **1930**, 861. See also French Pat. 669,643, Feb. 14, 1929; *Chem. Abst.*, **1930**, 1866. Cf. para 5274.

⁵¹ Marshall, *J. Physical Chem.*, 1926, **30**, 1634; *Brit. Chem. Abst.*, 1926, 216A. Cf. Jaeger. The reduction of carbon monoxide to formaldehyde and methanol at atmospheric pressure. *Abhandl. Kennt. Kohle*, 1926, **7**, 51.

⁵² Bredig and Carter, *Chem. Zeit.*, 1915, **39**, 72; *J.S.C.I.*, 1915, **34**, 278.

⁵³ Brit. Pat. application 278,353, convention date, Sept. 28, 1926, to Delco Light Co., assignees of Bichosky; *Chem. Age* (London), 1927, **17**, 515.

^{53a} Brown and Galloway, *Ind. Eng. Chem.*, 1930, **22**, 175. Preparation of methyl ether from oxides of carbon by means of catalytic hydrogenation, see Ullrich, *Metallbörse*, 1929, **19**, 1741–2; *Chem. Abst.*, **1929**, 5158.

200 atmospheres (generally 50–150) in the presence of substances capable of forming acetates which decompose with the formation of acetic acid at 400°–450° (preferably 200°–300°). When these substances are themselves capable of effecting the combination of carbon monoxide and hydrogen, they may be used alone; otherwise they must be used together with such substances, other than zinc oxide, as are employed in combining these gases to form oxygenated organic compounds. Catalysts which may be used are oxide of tin, copper, etc., copper acetate, methoxides of aluminum, etc., either alone or mixed with one another or with potassium or sodium acetate or methoxide, etc.⁵⁴

5563. In another method by Dreyfus⁵⁵ methanol is heated with carbon monoxide at atmospheric pressure in presence of substances which are, or form, acetates that split off acetic acid at temperatures below 450° C. Hydrogen may be present and, with excess methanol, methyl acetate is produced. Suitable catalysts are: oxides of copper, tin, lead or zinc; zinc acetate, zinc methylate, aluminum methylate, tin methylate; finely divided zinc, aluminum or copper; mixtures of sodium acetate and potassium acetate or mixtures of alkali methylates and other metal methylates. Temperatures of 200°–350° C. are preferable and the process may be carried out in a circulating system.

5564. Synthesis of Acetic Acid and Acetates. Smith⁵⁶ describes the manufacture of alkali acetates by reaction between methanol and sodium formate or between methanol, carbon monoxide and sodium hydrate or carbonate. The formate may be the crude product obtained by the action of the monoxide on caustic soda. The methanol may be in the form of vapor mixed with hydrogen and carbon monoxide as in the methanol synthesis. *Examples:* (1) Sodium formate with a little water is treated at 250°–300° C. with a stream of methanol vapor; (2) carbon monoxide or gas containing it is forced into an autoclave containing crude methanol and caustic soda or soda-ash until the pressure is about 50 atmospheres; the autoclave is then heated for two or three hours and the product worked up for sodium acetate or for acetic acid.⁵⁷

5565. A method of manufacturing acetic acid by heating a mixture of carbon monoxide and methanol under high (100–300 atmospheres) pressure at 300°–400° C. in presence of catalysts such as ortho-, pyro-, or metaphosphoric acid and other specified inorganic acids, is described;⁵⁸ one modification replaces preformed methanol by adding hydrogen which combines with the carbon monoxide to form methanol.⁵⁹

5566. Methanol from Methyl Formate.⁶⁰ One proposal is for the manufacture of methanol from methyl formate by the following process: A mixture of hydrogen, or a gas containing it, and methyl formate vapor is passed at normal pressure and at 100°–180° over a catalyst containing copper. Thus a mixture of 132 g. of the ester and 25 liters of hydrogen per hour was passed through a tube containing fragments of porous pot treated with the catalyst, and at 160° a mixture of hydrogen, 60 g. of unchanged ester, and 72 g. of methyl alcohol resulted, the two former being once more employed. The yield was some 90 per cent of that calculated from the formic acid. Water-gas may be used instead of hydrogen. Decomposition of the ester is more rapid, and can be performed in a smaller apparatus when this method is used than by earlier processes.⁶¹

5567. Formic Acid Esters. The process described below, though not a hydrogenation, has immediate relevance. Carbon monoxide, in the presence of water, is allowed to act on alcohols at raised temperatures with or without increased pressure and catalysts. Methyl formate is formed below 200° under ordinary pressure on leading carbon monoxide, methyl alcohol vapor, and steam over a variety of contact substances including such as favor the taking up and splitting off of water, but the reaction is greatly accelerated by increased pressure. Excess of alcohol improves the yields. For example, a mixture of carbon monoxide and methyl alcohol vapor in approximately the proportion 1 : 2 with steam when once led over titanium or thallium oxide, under ordinary pressure, at 175°, gives 0.1 per cent of methyl

⁵⁴ Dreyfus, Brit. Pat. 262,832 1925. *Brit. Chem. Abst.*, 1927, 125B; see also Dreyfus, Brit. Pat. 264,558, 1925; *Brit. Chem. Abst.*, 1927, 268B.

⁵⁵ Brit. Pat. 268,845, Nov. 7, 1925; *Chem. Abst.*, 1928, 22, 1365.

⁵⁶ Brit. Pat. 271,589, Mar. 13, 1926, to Synthetic Amm. & Nitrates, Ltd., and P. A. and H. G. Smith.

⁵⁷ *Chem. Age* (London), 1927, 17, 38.

⁵⁸ Brit. Pat. 283,989, July 20, 1926, to British Celanese, Ltd., and Dreyfus and Bader.

⁵⁹ *Chem. Age* (London), 1928, 18, 203.

⁶⁰ French Pat. 581,175, Aug. 7, 1913, to the Soc. chim. des Usines du Rhône. See para. 5571.

⁶¹ *Brit. Chem. Abst.*, 1927, 156B.

formate. Using zinc and manganese as contact substances with highly activated carbon as carrier, the yield is 1.0 per cent at 260°. With activated carbon at 200° and 200 atmospheres pressure, the yield of methyl formate rises to 12 per cent. Similar results are obtained with other alcohols.⁶²

5568. Motor Fuel Process. Air and steam are passed through a generator containing red-hot carbonaceous material; the carbon monoxide, hydrogen, and undecomposed steam produced are led through a bed of tin plate or other metallic scraps resting on a grate above the fuel. The gases then pass through the tubes of a steam boiler to closed coils in a still containing crude petroleum or heavy paraffin oils. The distillate is collected in a tank, where it is admixed with the cooled gases under pressure, yielding a motor fuel.⁶³

5569. Somewhat comprehensive claims are made by Aarts.⁶⁴ Active carbon is heated with hydrogen or hydrogen-containing gases at 150°–600° C., with or without a catalyst at atmospheric or slightly plus pressure. Nickel is a suitable catalyst. At 150°–400° C. saturated and at 400°–600° C. unsaturated hydrocarbons are the chief products.

Solid fuels may be gasified to produce a carbon monoxide-containing gas, which is then heated to 300°–500° C. The decomposition may be started by a catalyst such as iron, nickel, or cobalt oxide.

Hydrocarbons adsorbed in carbon may be used as fuel in internal combustion engines.⁶⁵

5570. Hansen ⁶⁶ obtains liquid hydrocarbons by subjecting carbon or the vapor of hydrocarbons, such as naphthalene (which need not be purified), at atmospheric pressure, to the action of hydrogen immediately after it has been dissociated by an electric arc or hot spark discharge. A catalyst may be used.

5571. Methanol from Alkyl Formates. Christiansen ⁶⁷ produces methanol from an alkyl formate (methyl formate) by the action of hydrogen in presence of a catalyst. Reduced copper is a suitable catalyst and the recommended temperature of operation is 180° C.⁶⁸

REFERENCES

5572. Neumann and Biljevic. Catalytic formation of formaldehyde. *Z. angew. Chem.*, 1927, **40**, 1469; *Chem. Abst.*, 1928, **22**, 760. As predicted by theory only traces of formaldehyde are formed in carbon dioxide-hydrogen mixtures at varying temperatures and with or without catalysts.

5573. Sabalitscha and Harnisch. Synthesis of formaldehyde and acetone from oxides of carbon and hydrogen or water through contact substances. *Biochem. Z.*, 1927, **190**, 265; *Chem. Abst.* 1928, **22**, 1571. Demonstrable quantities of these products are formed at 300° C. in contact with a great variety of substances, e.g., calcium carbide, silica, kaolin, iron, sodium hydroxide, charcoal, etc.

⁶² Ger. Pat. 422,500, Mar. 9, 1923, to Farb. vorm. Meister, Lucius and Brünig, assignees of Ernst and Sponsel.

⁶³ Hirsh, Brit. Pat. 258,913, May 5, 1925; *Brit. Chem. Abst.*, 1926, 1006B.

⁶⁴ Brit. Pat. 278,745, Oct. 7, 1926, to Aarts, assigned to Gen. Carbonalpha Co.

⁶⁵ *Chem. Abst.*, 1928, **22**, 2571.

⁶⁶ Brit. Pat. 284,224, Jan. 24, 1927.

⁶⁷ U. S. Pat. 1,302,011, Apr. 29, 1919. See para. 5566.

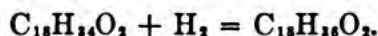
⁶⁸ Cf., Christiansen. Equilibrium between methyl formate and methanol and some related equilibria, *J. Chem. Soc.*, 1926, 413.

CHAPTER LVI

HYDROGEN (I)

THE HYDROGEN PROBLEM IN GLYCERIDE OIL HARDENING

5600. Oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the reaction:



Thus 282 lb. of oleic acid require 2 lb. (or about 0.7 per cent) of hydrogen for the production of 284 lb. of stearic acid, and similarly the transformation of olein into stearine requires the use of about 0.68 per cent hydrogen.¹

5601. One thousand cubic feet of hydrogen weigh approximately 5.6 lb., hence a pound of olein calls for a little over 0.1 of an ounce of hydrogen equivalent to approximately 2500 cu. ft. of hydrogen per ton (of 2000 lb.) of olein. Thus by weight only a relatively small quantity of hydrogen is needed, while by volume the amount required, of course, is considerable.²

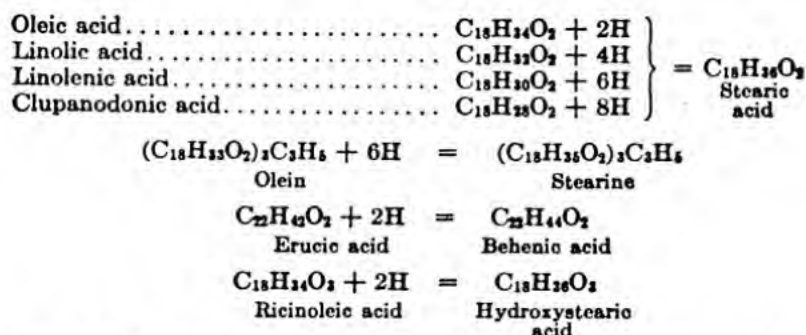
5602. The following tabulation shows the nature of the reaction in several cases:

¹ The amount of hydrogen required for complete conversion is given by Sachs (*Zeitsch. f. angew. Chem.*, 1913, 94, 784) as 7.4 kilos or 85 cu. m. hydrogen per 1000 kilos oleic acid. One thousand kilos of linoleic acid having two double bonds call for 14.2 kilos, or 170 cu. m. of hydrogen. One thousand kilos of linoleic with three double bonds need 21.6 kilos, or 289 cu. m. of hydrogen, while a like weight of clupanodonic acid with its four double bonds requires 29 kilos, or 349 cu. m. of hydrogen. The hydrogen requirements per ton of some of the fats enumerated by Sachs are as follows:

	Cubic Meters
Cocoanut oil.....	7.8
Tallow.....	33.57
Olive oil.....	68.80
Oleic acid.....	88.80
Corn oil.....	143.75

Dr. Holde observes (*Seifen. Ztg.*, 1912, 918) that oleic acid requires only 2 parts of hydrogen to 282 parts of oil in order to get stearic acid, while linoleic and linolenic acid require 4 and 6 parts respectively to 280 and 278 parts. Ricinolic acid, which contains 1 atom of oxygen more than oleic acid, forms an oxystearic acid which has a very high melting-point, but which also only contains 2 atoms more of hydrogen than the original acid. The glycerides of stearic or palmitic acid naturally remain unchanged throughout the operation.

² According to Linde (Production of Hydrogen, Third Int. Cong. of Refrigeration, 1913), 6 to 10 cu. m. of hydrogen are required for hardening 100 kilos of oil.



5603. One of the chief problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The two methods hitherto most favored in the hydrogenation of oils have been the iron-sponge steam process and the electrolytic method. For large plants the iron-sponge steam process has been preferred, but it is relatively complicated and scarcely to be recommended for plants calling for 1000 cu. ft. of hydrogen, or less, per hour.

5604. In the electrolysis of brine to make caustic soda and bleach, there exists a by-product of hydrogen sufficient in amount to treat an enormous quantity of oil or conduct other hydrogenation operations on the large scale. To-day a good portion of this hydrogen is being used in various hydrogenations.¹

5605. Use of "Hydrogen-containing Gases." This expression is often used. The reference usually is to such products as coke-oven gas and water-gas. Coke-oven gas contains about the following:

	Per Cent
Hydrogen	46
Nitrogen	15
Carbon monoxide	7
Methane	20
Ethylene	2
Carbon dioxide	4

This gas may be obtained in large quantities at low cost in the neighborhood of coke-oven plants. Many of the patents relating to the hydrogenation of oils refer to the use of gas mixtures containing hydrogen as well as to hydrogen gas in a pure state.

5606. Carrying out the hydrogenation process with hydrogen-containing gases involves: (1) the catalyzer must not become contaminated with poisons; (2) the process must proceed in spite of the presence of foreign gases; (3) foreign gases must not injure the oil.

5607. Nitrogen does not injure the ordinary catalysts but acts as an inert diluent. The same is true of carbon dioxide. The monoxide is objectionable in that it reduces the activity of some catalysts. Sulphur compounds poison the

¹ Similar conditions exist abroad, Blum reporting (*Met. and Chem. Eng.*, 1911, 157) that enormous amounts of hydrogen gas are produced in large works for the production of caustic soda and chlorine by electrolysis of common salt solutions. The hydrogen gas is set free together with the caustic soda at the cathode. In this case the cost of the gas is practically that of its compression and storage. Special railway cars are built in Germany for the transportation of 500 cylinders containing 2750 cu. m. of hydrogen gas. The cost of shipment of the cylinders is so great that the distribution, of course, is only local, as regards consumption on the large scale. The Zeppelin Garage in Frankfort is supplied with hydrogen by means of a high-pressure main from Griesheim.

catalysts used in oil hardening and, with few exceptions, those used in other hydrogenations. With circulating gases, the hydrogen being absorbed, the inert constituents accumulate until their proportion is so large as to render it necessary to discharge the gas.

5608. According to Walker, when water-gas is used in oil-hardening, only about one-third of the contained hydrogen or approximately 17 per cent of the total gas is used. To secure the same effect 600 cu. ft. of water-gas in place of 100 cu. ft. of hydrogen are required, in which case about 500 cu. ft. of spent gas results. The spent gas, of course, should not be thrown away as this would be wasteful and arrangements must be made for its use in heating, lighting or power applications. It is not always convenient to thus make use of such a large volume of hydrogen-spent gas; furthermore, it is necessary to make all the pipes and connections larger by sixfold than when concentrated hydrogen is employed, which means an additional expense.

5609. Finally there is the question as to whether or not the foreign gases⁴ contained in water-gas exert any detrimental influence upon the hardened oil; whether they do not during the process bring about side reactions. As regards carbon monoxide⁵ and carbon dioxide no chemical action on oils or fatty acids under these conditions is known, yet eventually catalyzers may be employed which cause side reactions. Thus when using water-gas in place of hydrogen, a number of difficulties are likely to arise in large scale operation and the seeming financial advantage on close inspection shrinks considerably, practically leaving the field to technically pure hydrogen.

SOURCES OF INDUSTRIAL HYDROGEN

5610. The practically available sources of hydrogen may be classified as follows:

A. From Coal. *Water-gas:* (1) Steam-iron process; (2) catalytic process; (3) lime process; (4) liquefaction process.

Coke-oven gas: Liquefaction process.

B. From Hydrocarbons: (1) By thermal decomposition; (2) by interaction with steam; (3) by interaction with carbon dioxide; (4) by partial combustion.

C. From Water: (1) By electrolysis; (2) Bergius process; (3) various other less important processes.

D. The Phosphorus Process.

E. Miscellaneous Processes, including the ferrosilicon process and those in which hydrogen occurs as a by-product.

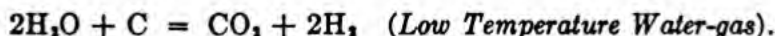
⁴ The addition of small quantities of a second gas to a pure gas markedly reduces the rate of diffusion in liquids, according to Barus (*Chem. Abst.*, 1913, 3871).

⁵ Caro (*Seifen. Ztg.*, 1913, 852) considers the presence of carbon monoxide in hydrogen used for hardening fats with nickel catalyzers to be, under some circumstances, injurious to the catalyzer. Maintaining the temperature of the oil during hydrogenation above 200° C. is said to be beneficial, as any nickel carbonyl formed will be at once decomposed at that temperature. Maxted points out the slowing up of oil hardening which results from the presence of carbon monoxide. This is objectionable in hydrogenating for edible fat because long operation time tends to spoil flavor. (*Trans. Faraday Soc.*, 1917, September.) High operation temperature has a similar effect on flavor.

WATER-GAS

5611. When steam interacts with carbon at high temperatures the following reaction occurs: $\text{H}_2\text{O} + \text{C} \rightleftharpoons \text{CO} + \text{H}_2$. This is the reaction of the ordinary technical method for the manufacture of water-gas and it takes place at about 1000°C . (*High Temperature Water-gas*.)

5612. If means (e.g., catalysis) be found to bring about the reaction at a lower temperature (below 800°C .) the course of the reaction tends to run:

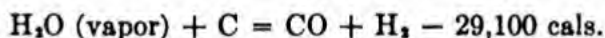


This has been realized in practice in two ways: (1) the Bergius process in which carbon is heated with water at 300°C . under pressures sufficient to keep the water liquid



(2) by mixing catalysts (e.g., lime) with the coke, whereby the reaction temperature is lowered to 500° – 600°C .

5613. The usual, almost invariable technical practice is to make water-gas by the high-temperature method. Alternate blasts of air and steam are blown through a bed of hot coke. During the air blasting a high temperature is reached. The flue gases are low in caloric value. During the steaming the fuel gradually falls in temperature its heat serving to supply the energy for the reaction:



The gases from the air blasting are collected separately from those of the steaming. These latter, only, are water-gas.

The composition of the effluent varies with the temperature at which it has been produced. However, owing to the much greater velocity of the reaction at high temperature, the average water-gas obtained has the character of a high-temperature product.

5614. The following table * shows the effect of temperature both on the velocity of the reaction and on the composition of the product.

Temperature, $^\circ\text{C}$	Per Cent of Steam Decomposed	Composition by Volume of Gas Produced		
		Hydrogen	Carbon Monoxide	Carbon Dioxide
674	8.8	65.2	4.9	29.8
758	25.3	65.2	7.8	27.0
838	41.0	61.9	15.1	22.9
954	70.2	53.3	39.3	6.8
1010	94.0	48.8	49.7	1.5
1125	99.4	50.9	48.5	0.6

* From Teed, *Chemistry and Manufacture of Hydrogen*, originally from Bunte, *J. für Gasbeleuchtung*, **37**, 81.

5615. Inspection of these results shows that at 1000° C. about equal volumes of hydrogen and of carbon monoxide are produced, i.e., the equation: $C + H_2O = CO + H_2$ is realized. At the lowest temperature (674° C.) the product is approaching the proportions two-thirds hydrogen, one-third dioxide, corresponding to: $C + 2H_2O = CO_2 + 2H_2$.

WATER-GAS MANUFACTURE

5616. We do not intend to describe in any detail the appliances and methods used in water-gas manufacture, but to give some general information on the subject.

5617. In the early days of water-gas manufacture the generator was externally heated. Nowadays the heat is obtained by partial burning of the fuel inside the generator either by the English (deep fuel bed) or the Swedish (shallow fuel bed) method.

5617A. A return to the original external heating is proposed by Bellay⁷ probably to avoid the dilution of the product with nitrogen. Water-gas is produced by gasification of coke, lignite, turf and other fuel rich in carbon without admission of outer air, within a generator heated from the outside, into which superheated steam is blown. The gas produced is enriched in hydrogen by causing it to flow through a column forming an extension of the lower generator with adjustable heating and having partitions of fireproof clay and coal and blowing into the column superheated steam at 100°–400°. The enriched gas is brought into a purifier and condenser containing lime milk in which the carbon dioxide and coal dust and impurities are separated, the remaining gases being brought to a purifier heated from outside and filled with a fresh preparation of soda-lime and completely retaining all the carbon monoxide and carbon dioxide still remaining in the hydrogen. The pure hydrogen is passed to a gasometer.

5618. As we have said, in the English method the fuel bed is deep, in the Swedish method it is shallow. The consequence of the English way of working is that the carbon dioxide, formed by the combustion of the coke during the air-blasting, becomes reduced to monoxide as it traverses the deep bed. This is not an advantage because, at best, the proportion of monoxide will not exceed 30 per cent, the rest being chiefly nitrogen.

5619. In the Swedish way of working the carbon dioxide has no chance to be reduced and the heat loss is saved. Therefore the coke mass gains the necessary high temperature quickly and the air-blasting time is reduced.

5620. A modern water-gas generator is a cylindrical structure with a hearth below and a charging orifice above. The latter is provided with a lid. There is an upper and a lower steam inlet and upper and a lower gas outlet. These are used in pairs, alternately, the upper steam inlet with the lower gas outlet and *vice versa*. This insures even distribution of heat through the fuel. Fire having been made on the hearth, the generator is charged from the top, the lid of which is left open during the air-blowing. Steam inlets and gas outlets being closed, air is blown in at about 15 ins. plus pressure of water. The gases (ideally 20 per cent carbon dioxide, 70 per cent nitrogen, etc.) escape through the open lid.

⁷Can. Pat. 282,952, Sept. 4, 1928; *Chem. Abst.*, 1928, **22**, 4213. Brit. application, 284,262, convention date, Jan. 26, 1927; *Chem. Age* (London), 1928, 305.

When a temperature of about 1000° C. has been attained, air is shut off, the lid is closed, one steam inlet and the corresponding gas outlet are opened, and steam is admitted at 120 lb. per sq. in. When the temperature falls to the economical limit, the operation is recommenced, except for the fuel charging which occurs only after the third steaming which completes the cycle.

5621. With a generator having a hearth 5 ft. 6 in. in diameter such a cycle would be as follows: ⁸

Air blast.....	2 minutes
Steam upwards.....	6 minutes *
Air blast.....	1 minute
Steam downwards.....	6 minutes
Air blast.....	1 minute
Steam upwards.....	6 minutes

After this a fresh fuel charge would be added and the cycle recommenced.

5622. Various methods of construction are used to make the working more uniform and more nearly continuous. Such are devices for maintaining uniform feed and height of fuel, for declinkering, etc. For these the reader is referred to manuals on fuel technology.

5623. Apparatus for Making Water-gas. The generating chamber has a grate containing passages connected with a pipe through which water is supplied for the purpose of generating and superheating steam. The steam is discharged through an outlet below the grate and passes upwards, through the grate, to the fuel bed.⁹

5624. Leonars¹⁰ makes water-gas by causing steam and carbonaceous material to meet in a bath of molten metal (iron). The gases pass up through the charge. The slag is withdrawn from the surface of the metal from time to time. Instead of solid fuel, liquid hydrocarbons may be used.

5625. Composition of Water-gas. With coke containing about 83 per cent of carbon, 6.0 per cent of moisture and 9.0 per cent of ash, the water-gas would have about the composition: ¹¹

	Per Cent by Volume
Hydrogen.....	52.0
Carbon monoxide.....	39.6
Methane.....	0.4
Carbon dioxide.....	3.5
Hydrogen sulphide.....	0.5
Nitrogen.....	4.0

Approximately 45 per cent of the carbon of the coke is present in the water-gas. Owing, however, to the high calorific value of the gas the efficiency of the process works out at 66 per cent.

5626. The subsequent treatment of the water-gas depends on the process in which it is to be used. For the carbon monoxide syntheses it undergoes purification and partial conversion, so that the necessary ratio—hydrogen : carbon monoxide—may be obtained, a ratio which varies according to the nature of the prod-

⁸ Teed, *loc. cit.*

⁹ U. S. Pat. 1,592,464, July 13, 1926, to McDonnells; *Brit. Chem. Abst.*, 1926, 813B.

¹⁰ U. S. Pat. 1,592,861, July 20, 1926. Apparatus described and illustrated.

¹¹ Teed, *loc. cit.*

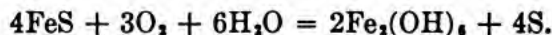
uct desired. For hydrogenation of oils and for most organic hydrogenations it is, after purification, subjected to one of the processes about to be described in order to obtain pure hydrogen or, at any rate, to remove catalyst poisons and carbon monoxide.

PURIFICATION OF WATER-GAS

5627. Removal of Mechanical Impurities. As it comes from the generator water-gas contains ash and dust. These are removed by passing the gas up through a tower where it meets a down-flowing current of cold water. This scrubbing process also removes most and usually all of the iron carbonyl present.

5628. Gaseous Impurities. The noxious impurities that may be present in crude water-gas are: Sulphur compounds (hydrogen sulphide, carbon disulphide, carbonyl sulphide and thiophene), and iron carbonyl. There is also a small quantity of methane which is harmless for most technical organic hydrogenations. If the gas is intended for maximum conversion to hydrogen by the catalytic, the steam-iron or the Griesheim (lime) process it is not essential to give it a preliminary purification since each of these processes effects this. If it is intended for use in the methanol and similar syntheses it must be purified. Even for the catalytic process this is desirable if certain active but easily poisoned catalysts are used.

5629. Removal of Sulphuretted Hydrogen. This has been very thoroughly worked out in a century and more of coal gas practice. The purification is usually effected by passing the gas, preferably at 12°–20° C.¹² over hydrated oxide of iron. When the hydrated oxide loses its efficiency the gas is sent through another purifier and the contents of the first are exposed to the open air. By the action of water and air the following reaction is caused:



The original hydroxide is regenerated and is ready for re-use. This cycle can be repeated until the sulphur content rises to 50–60 per cent. The product can then be sold to manufacturers of sulphuric acid. One ton of oxide will purify about 2,000,000 cu. ft. of gas.

5630. Another method of removing hydrogen sulphide is suggested by Laryokov.¹³ The gas is passed up a coke-filled tower where it meets and is scrubbed by a cold 5–10 per cent solution of sodium or potassium carbonate. The sulphide is absorbed with formation, e.g., of sodium hydrosulphide and bicarbonate. The carbonate and hydrogen sulphide are regenerated by blowing with hot air which carries off the sulphide.

5631. Removal of Organic Sulphur Compounds from Hydrogen, etc. According to Fischer and Tropsch¹⁴ hydrogen may be purified from sulphur-containing organic compounds by passing the mixed gases over a catalyst consisting of

¹² In climates where very low temperatures are experienced means of heating the oxide mass must be provided, e.g., by steam pipes.

¹³ *Masloboino Zhirovoe Delo, Oil and Fat Ind.*, Russia, 1928, No. 2, 6–7.

¹⁴ Brit. Pat. 254,288, June 3, 1926; *Brit. Chem. Abst.*, 1927, 385B.

finely divided lead or tin or alloys thereof, deposited upon an inorganic substance (e.g., bases or acid anhydrides) which remains solid at the temperature of reaction, i.e., above the melting-point of the metallic catalyst. Such a contact material, consisting of equal parts of lead chromate and copper oxide treated with hydrogen at 400°, is able at 300°–500° and ordinary pressure to desulphurize gas and maintain its activity for several months.

5632. Removal of Iron Carbonyl. A Badische Co.¹⁵ process for removing carbonyl from gaseous mixtures is especially intended for gases to be used in the methanol and related syntheses. The gases are mixed with a measured quantity of air or of hydrochloric acid gas and the mixture is passed over a layer of activated carbon. The iron carbonyl is decomposed with formation of oxide or chloride. The carbon can be revived by treatment with acid and washing.

5633. Sulphur, phosphorus and arsenic present as organic compounds in hydrogen mixtures may be removed by passing the gas, at 200°–500° C. and under a pressure of 100 atmospheres, over a catalyst comprising metals, other than copper, having an atomic weight between 51 and 65, or oxides of metals such as nickel and alumina. Impurities are converted by this treatment into methane and homologs and inorganic compounds of sulphur, etc., which latter may be removed by alkali.¹⁶

5634. In another process the gas or gas mixture receives alternate and repeated treatment first with alkali to remove carbon dioxide, hydrogen sulphide, sulphur dioxide, etc., then under 70–800 atmospheres pressure at 150°–450° C. with catalysts similar to those described in the last paragraph.¹⁷

5634A. A process described by the Stoltzenberg Company¹⁸ is intended for the separate production of carbon monoxide and of hydrogen. The carbon monoxide contained in water-gas after purification by the usual means, is absorbed by cuprous chloride solution, and from this solution pure carbon monoxide is liberated by ordinary methods. The hydrogen freed from the remaining traces of carbon monoxide by passing it over heated iron oxide, is finally cooled and washed to remove the aqueous vapor and carbon dioxide. The reduced iron is reconverted into the oxide by treatment with steam.

THE STEAM-IRON PROCESS

5635. When steam is passed over heated iron it is decomposed, the iron is oxidized, and hydrogen is produced.



5636. Theoretically, 1000 cu. ft. of hydrogen, measured at 760 mm. and 14.5° C., should be formed by the action of 49.95 lb. of steam on 116.5 lb. of iron. This yield is not nearly attained in practice.

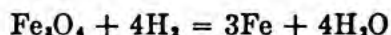
¹⁵ Brit. Pat. 247,050, May 21, 1925.

¹⁶ Brit. Pat. 276,687, Aug. 30, 1926, to Gewerksch. Steinkohl. Mont-Cenis.

¹⁷ Brit. Pat. 276,668, Aug. 26, 1926, to the same patentees.

¹⁸ Ger. Pat. 44,911, July 12, 1924, to Chem. Fabr. H. Stoltzenberg.

5637. After the reaction, which is superficial, has ceased, the iron is regenerated by passing water-gas over it.



The cycle can then be recommenced.

5637A. Loshkarev¹⁹ has observed that in the reduction phase, the carbon monoxide enters sooner into the reaction and that a disproportionate amount of it is consumed. The larger the proportion of monoxide present in the water-gas, the shorter is the reduction time. Loshkarev therefore recommends increasing the proportion of monoxide either by injection into the water-gas producer of gas already used in reduction or by addition of oxygen to the air used for combustion. In either case the effect is to add carbon dioxide to the gases in the generator.

5638. The steam-iron process has been applied on an enormous scale, especially in the production of hydrogen for the hardening of oils. It is threatened by the newer processes, but is still used and new plants to work it are still being installed. In some forms the hydrogen it yields is not sufficiently free from carbon monoxide to cause that rapid hardening which is desirable in the preparation of edible oils. This disadvantage, however, has been overcome. Maxted claims to produce, by his modification, a gas as pure as electrolytic hydrogen.

5639. At the outset the generator is not charged with metallic iron. In fact there is never a great quantity of metal present. As usually worked, a generator will run through two complete cycles in one hour. Yet to produce 3500 cu. ft. of hydrogen (in two cycles) per hour, 6 tons of oxide are required.²⁰ We have seen that the theoretical quantity of iron which corresponds to 1750 cu. ft. (one cycle yield) is about 200 lb. The generator is charged with some such iron ore as hematite, then, at a temperature of 650°–900° C., water-gas is passed over the ore to reduce it superficially. This method produces a shallow film of spongy iron on the surface of the oxide. The latter, being robust and refractory, possesses considerable resistance to disintegration. In this way the passage for the gas is kept clear. If the temperature is allowed to go higher than 900° C. there is a tendency to sintering, producing an obstruction to the flow of gas and steam.

5640. When the reducing stage is finished it is necessary to flush out the generator to remove the residual water-gas. This operation, termed purging, takes only a few seconds. The gas so removed can be stored and burned, or used in some other way.²¹

5641. There are thus three periods in a cycle of operations: reducing, during which water-gas is passing over the ore; purging; and oxidizing when steam is

¹⁹ *Oil and Fat Ind.*, Russia, 1926, **6**, 22; *Chem. Abst.*, 1928, **22**, 3741.

²⁰ Teed: *The Manufacture of Hydrogen*.

²¹ The waste gases from each phase of the process may be collected in a common container and used as heating gas. Small quantities of the reducing gases used in the process may be added. (Ger. Pat. 466,109, Dec. 24, 1926, to Bamag-Meguine, A.-G.; *Chem. Abst.*, 1929, **23**, 942.)

passing and hydrogen is being evolved. According to Teed (*loc. cit.*) the durations of these stages are: reducing, 20 minutes; purging, 35 seconds; oxidizing, 9 minutes 25 seconds.

5642. A representative sample of gas obtained will have the following composition ²² (Teed, *loc. cit.*).

	Per cent by Volume
Hydrogen	97.5
Carbon dioxide	1.5
Carbon monoxide	0.5
Hydrogen sulphide	0.03
Nitrogen	0.47
	<hr/>
	100.00
	<hr/>

5643. Purification of the Gas. Water scrubbing serves to remove the dust, etc., and also some of the carbon dioxide. The gas is then passed through an iron oxide purifier to remove hydrogen sulphide and next through a lime box to take out the carbon dioxide.

5644. Deterioration of the Ore. Although, as we said, the ore is robust, nevertheless, with time it tends to disintegrate, breaking up into small fragments and offering undue resistance to the flow of gas. This necessitates replacement by fresh ore. Another cause of deterioration is sintering which, indeed, is believed by many to be the fundamental cause. A number of suggestions have been put forward to overcome this difficulty. They are of two kinds. Either the ore is to be mixed with some substance which will render it more refractory, or catalytic substances are added to reduce the working temperature.

5645. Messerschmitt employs spongy iron produced from fragmentary oxide iron ore (i.e., an ore containing Fe_2O_3). Only spongy iron produced from such oxidized iron ore is regarded by Messerschmitt as possessing the requisite porosity and strength for carrying out the process. The effect of using ferric oxide as raw material, it is claimed, is that the oxide after reduction becomes porous throughout its entire mass on account of the decrease in volume consequent upon the removal of the oxygen therefrom and thus an increased surface is exposed to the subsequent action of the steam. The use of ferric oxide in the form of oxide ores is important because the lumps of this ore, in consequence of its peculiar natural texture, maintain their shape in spite of repeated reductions and oxidations and the ore possesses the necessary strength to withstand the pressure of superimposed layers; if this were otherwise the path for the gases would become choked by the crumbling of the ferric oxide and continuous working would be impeded. The gangue, clay, silica and other components of the ore have for effect to prevent (in spite of high temperatures which may be produced either intentionally or in consequence of irregular working of the furnace) a sintering of the charge, the latter thus constituting a sort of rigid incombustible carrier for the oxides and the iron sponge.²³

5646. Natural ores of manganese or of manganese and iron are employed by Messerschmitt in place of ordinary iron ore. It is stated that hydrogen is obtained in good yields at 700° to 800° C. or about 200 degrees lower than with iron sponge.²⁴

²² The John Thompson Co., of Wolverhampton, who exploit the Maxted process, state that, with the ordinary steam-iron process, a monoxide content of 2 per cent is common. For certain purposes, e.g., aeronautics, the low nitrogen content gives this process considerable advantage over some of its competitors.

²³ U. S. Pat. 971,206, Sept. 27, 1910.

²⁴ French Pat. 461,480, 1913.

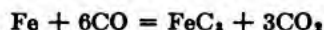
5647. Messerschmitt also recommends as a contact material a mixture of spongy iron and manganese, cobalt or nickel. The mixture may be made by adding the other metal to the spongy iron and is used in powder form or molded into briquettes, or natural ores containing these metals may be used. This mixture has the advantage of not being easily poisoned and may be worked at a lower temperature. Manganese is of special value if a gas containing carbon is used in the reduction stage, for manganese dioxide in the presence of carbon, oxidizes the latter.²⁵

5648. Dieffenbach and Moldenhauer²⁶ use the residue left on roasting spathic iron ore in the air in the preparation of iron to be employed in the decomposition of steam. This material is very porous, and is in most cases free from substances which would have injurious effects in the manufacture of hydrogen. They also claim the use of alloys of iron with manganese, chromium, tungsten, titanium, aluminum or other similar elements as the primary materials. These have the advantage that they are not fusible, do not soften, and do not form fusible or soft compounds with iron or its oxides. In place of alloys, mixtures of iron or its oxides with the other elements specified, or their oxides, may be employed, for instance in the form of briquettes.²⁷

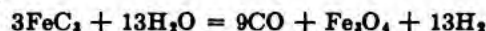
5649. Illuminating gas, water-gas or other gas containing free hydrogen, according to Jaubert, is passed through retorts packed with briquettes formed of iron oxide with a refractory substance and a catalytic agent, the retorts being heated to 800° to 900° C. Steam is afterwards passed through the retorts at the same temperature, yielding hydrogen. The briquettes are preferably composed of a mixture of 30 to 60 kilos of iron oxide (Fe₂O₃ or Fe₃O₄), 15 to 25 kilos of fire clay or pumice, 15 to 25 kilos of calcined magnesia and 5 to 15 kilos of the oxide of lead, copper, chromium or manganese.²⁸

5650. To prevent fritting the Badische Co.²⁹ proposed as remedies: the use of fused iron oxides, especially in conjunction with refractory and difficultly reducible oxides of high melting-point such as magnesia or zirconia, the iron oxides being prepared by the fusion of metallic iron in the presence of air or an oxidizing agent; fused iron oxides may be used in conjunction with a silicate as well as similar naturally occurring minerals such as magnetite. The Badische Co. also recommend spongy iron prepared by the reduction of minerals or oxides of iron by means of carbon, employing external heating. The metal is said to retain its porosity after repeated use. "Spongy Swedish iron," prepared in the above manner, is especially suitable.³⁰

5651. Temporary deterioration of the ore also happens, due to the reaction:



taking place toward the end of the reducing process. During the oxidizing stage another reaction *slowly* occurs:



This leads to a gradual increase in the quantity of carbon monoxide contained in the gas. To correct the defect a volume of steam may be added to the water-gas equal to one-half the volume of the contained carbon monoxide. While this slows up the reduction it does away with the carbide formation and increases the purity of the product.³¹

5652. According to Marted and Ridsdale³² hydrogen prepared by the steam-iron process contains considerable quantities of carbon monoxide, due to the deposition of carbon during the reduction and its subsequent oxidation, by the steam.

5653. Hydrogen free from carbon monoxide is obtained by employing for the reduction of the iron oxide a reducing gas containing substantially more carbon dioxide than carbon monoxide, a suitable ratio being 2 : 1. This may be obtained by adding carbon dioxide to water-gas, or by suitable modifications in the manufacture of the reducing gas, but dilution

²⁵ U. S. Pat. 1,109,448, Sept. 1, 1914.

²⁶ Ger. Pat. 232,347 of 1910.

²⁷ French Pat. 444,044, May 20, 1912. See also *Zeit. f. angew. Chem.*, 1914, 222.

²⁸ French Pat. 418,312 of 1909.

²⁹ French Pat. 440,780, Feb. 29, 1912.

³⁰ French Pat. 453,077, Jan. 11, 1913.

³¹ French Pat. 395,132 of 1908, to Dellwick-Fleischer Wassergas Ges. Partial reduction is also recommended.

³² Brit. Pat. 12,698; *Spet.* 4, 1915; *J.S.C.I.*, 1916, 1060; *Chem. Abst.*, 1917, 538.

of the gas with nitrogen (e.g., by partial combustion of the gas with air) or by steam must be avoided. The presence of carbon dioxide in the reducing gas prevents the deposition of carbon during the reduction of the iron oxide to iron, and, therefore, no carbon monoxide is formed when steam is passed over the heated iron to produce hydrogen.

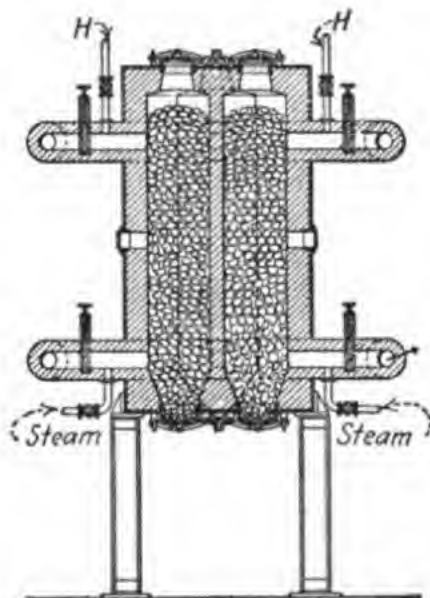


FIG. 148.

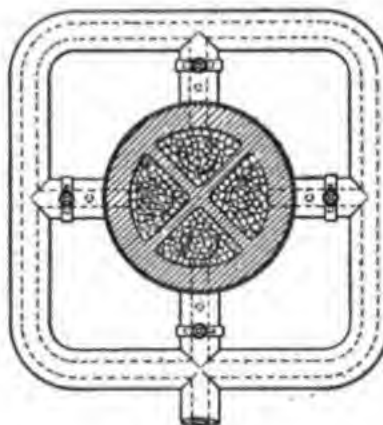


FIG. 149.

5654. Another remedy for carbon deposition consists in "burning" off the carbon by occasional admission of air. Unfortunately this tends to hasten the disintegration of the ore body.

5654A. Dicke ²² generates hydrogen by the action of steam on scrap from the various departments of an iron and steel works, and the resulting iron oxide is utilized in the blast furnace or open hearth furnace. The apparatus is constructed of a refractory chamber surrounded by a tight metal jacket. The chamber is divided into separate compartments by refractory walls. The compartments are arranged with valves, etc., so that they operate independently of each other. They are charged with iron ores or scrap iron and operated in the usual manner. The apparatus is shown in vertical section in Fig. 148 and in cross-section in Fig. 149.

5655. There are two general types of plant for the iron-steam process, the multiple retort system and the single retort system.

5656. Multiple Retort System.²³ The apparatus provided for operating this process consists of a combustion chamber containing a number of vertical retorts, the chamber being provided with a gas producer. A combustible gas is delivered from the producer and burned by means of secondary air in the combustion chamber around the outside of the retorts, the products of combustion passing away through recuperators to a stack. The retorts are charged with iron ore of proper grade and sufficiently porous in itself and of proper sized lumps to allow of a more or less free passage of gas. It is necessary that the greatest possible surface of ore be exposed. In operation the blue water-gas holder is filled, the hydrogen

²² Ger. Pat. 280,964, Aug. 14, 1913; Brit. Pat. 29,390, 1913; French Pat. 465,474, Nov. 28, 1913; U. S. Pat. 1,129,559, Feb. 23, 1915.

²³ Modified Lane Process of Improved Equipment Co., New York City.

retorts brought up to heat, and by means of suitable valve connections the steam and blue water-gas are alternately passed through the retorts, the resulting hydrogen passing to a holder and the products of combustion passing to the atmosphere. The retorts are usually made of cast steel, which seems to be as satisfactory as any material which has been used. Cast-iron retorts have been used with more or less success. The destruction of the hydrogen retorts appears to commence on their outside diameter, working inward more rapidly than from the inside outward. It is obvious that they should fail in this manner as the combustion surrounding the outside of the retorts continually cuts into them, whereas absorption by ferrous oxide of oxygen takes place more rapidly than the absorption of oxygen by metallic iron, and the entire charge of ferrous oxide is changed to the ferric condition before there has been time for the walls of the retorts to be seriously attacked by the oxygen of the steam.

5657. As it has been found in practice that the reducing reaction takes considerably longer than the generation of hydrogen, the Lane process may be carried out in three or more groups of retorts, the greater part of which are constantly subjected to the action of reducing gases for the regeneration of the iron, or other hydrogen-producing substance. The retorts communicate with one another by means of a series of pipes, fitted with controlling valves,

so that steam or the reducing gases may be admitted as required. The hydrogen, which is evolved in the first few minutes of the operation, being impure, is diverted from the collector of pure hydrogen, and mixed with the water-gas used for reduction. Means are provided for forcing hot air through the reaction chamber, which is done periodically between the two reactions so as to burn out objectionable impurities, especially sulphur.²⁴

5658. Lane²⁵ proposes means for removing the reducing gas as well as the sulphur, carbon and other impurities between the two oxidizing and reducing steps of the process. To this end the retort is provided at each extremity with a multiple-way controlling valve adapted to establish communication between that end of the retort and any one of three pipes connected respectively at the one end of the retort to a supply of air under pressure, a supply of reducing gas, and a hydrogen receiver, and at the opposite end of the retort respectively to an outlet, a gas-washing and regenerating apparatus, and a supply of steam under pressure.

5659. In Fig. 150, *A* is the retort provided with an inlet *B* at the lower end and an outlet *C* at the upper end, and *F* and *G* are four-way valves which are capable of being rotated by means of hand-wheels *H* and *J* so as to open communication on the one hand between the retort *A* and either the pipe *K* connected to a hydrogen container, a pipe *M* connected to a supply of reducing gas, or a pipe *N* connected to a supply of air under pressure, and on the other hand either with a discharge pipe *O*, a pipe *P* leading to a gas-washing or regenerating apparatus and a pipe *Q* connected to a supply of low-pressure steam. Assuming that the contact material in the retort has been oxidized during the previous hydrogen-producing phase, the sequence of operations is as follows: In the first place the impurities deposited on the contact material during the previous reduction phase, or present in the gaseous state in the retort, are removed by effecting their combustion. This is effected by rotating the valve *G* one-quarter of a revolution so as to admit air under pressure to the lower part of the retort

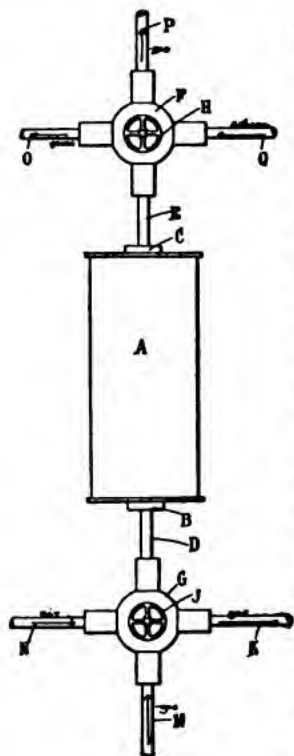


FIG. 150.

quarter of a revolution so as to admit air under pressure to the lower part of the retort

²⁴ Lane, Brit. Pat. 17,591, July 29, 1909; Brit. Pat. 11,878, Jan. 29, 1910.

²⁵ Lane, U. S. Pat. 1,028,366, June 4, 1912.

through the pipes *N* and *D*, and rotating valve *F* so as to force out the products of combustion into the atmosphere through the pipes *E* and *O*. The valve *G* is then rotated so as to admit reducing gas to the retort through pipes *M* and *D* and rotating valve *F* so as to open communication between the upper part of the retort and the gas-washing or regenerating apparatus through pipes *E* and *P*. At the completion of the reducing phase the valve *F* is rotated so as to connect the upper part of the retort with the supply of steam under pressure through pipes *Q* and *E*, whereupon the pressure of the steam being greater than that of the reducing gas remaining in the retort, the latter is forced out through pipes *D* and *M* carrying with it the impure hydrogen which has been generated by the action of the steam on the sulphur, carbon, etc., deposited on the contact material. As soon as it is found that the hydrogen passing out through pipe *M* is sufficiently pure the valve *G* is rotated so as to deliver the gas to the hydrogen container, after which, air is then again passed through the retort in the manner previously described.

5660. Lane ³⁶ purifies the reducing gas in the manufacture of hydrogen by the alternate oxidation and deoxidation of iron, by compressing the reducing gas to a pressure of several atmospheres and then causing it to flow (while still under pressure) in contact with an oppositely flowing stream of water. To increase the effectiveness of the washing operation, the gas is passed through a coke tower through which water is flowing in an opposite direction.

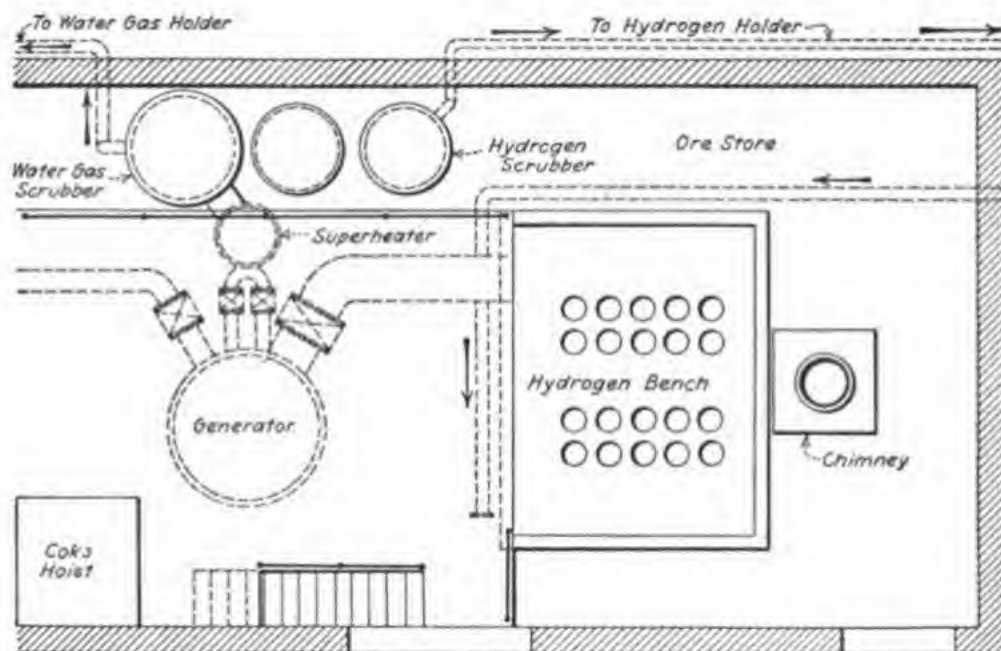


FIG. 151.

5660A. R. and J. Dempster, Ltd. (Manchester, England), have furnished hydrogenating equipment similar to that shown in Fig. 151. The plant consists of a blue water-gas equipment, water-gas holder, rotary exhaustor, steam engine and purifiers, a hydrogen bench (generators), hydrogen scrubber and purifiers and a hydrogen holder. Steam of 60 to 80 lb. pressure is used. The retorts of the hydrogen bench are heated by means of the blow gases of the water-gas generator.

5661. Single-Retort System. Messerschmitt ³⁷ has described a great variety of single-retort plants for the iron-steam process. One style of retort described by him consists of two cast-iron cylinders, one being so supported that it is free to expand

³⁶ U. S. Pat. 1,040,218, Oct. 1, 1912; Brit. Pat. 11,878, 1910.

³⁷ Brit. Pat. 18,942 of 1913.

upwards, the other able to expand downwards. The annular space between the two cylinders is filled with suitable iron ore, while the circular space inside the smaller cylinder is filled with a checkerwork of refractory brick. The plant is operated by first heating the refractory bricks by means of water-gas and air. The heating of the checkerwork is communicated by conduction to the ore mass; when this is at a suitable temperature (about 750°C.) the gas supply is shut and water-gas enters, passing up through the ore and reducing it. When the reducing gas reaches the top of the annular space it mixes with air entering by an inlet

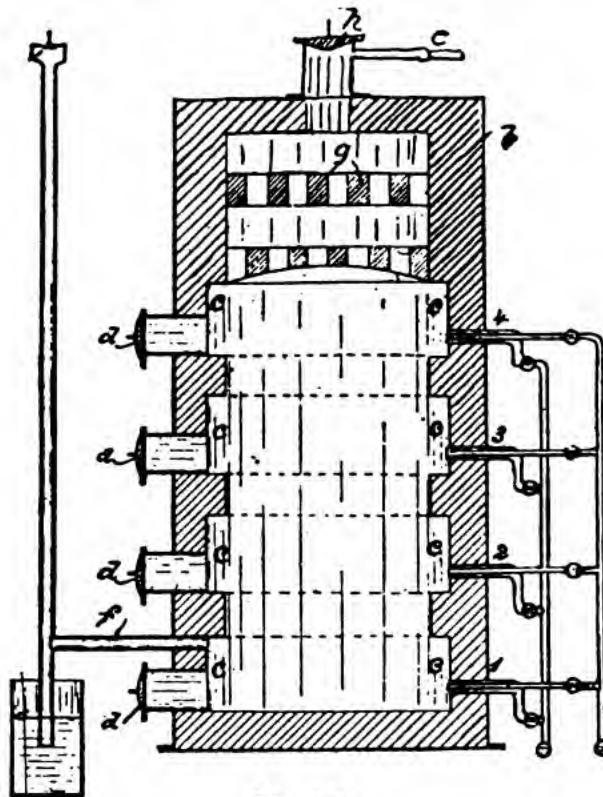


FIG. 152.

and the unoxidized portion burns, heating up the brickwork, and finally passing away to the chimney.

5662. When reduction is complete (after about twenty minutes) the gas inlets are closed, and steam is admitted. This passes upwards through the checkerwork becoming superheated, and then down through the contact mass where it is decomposed, producing hydrogen, which passes out through a water seal and thence to a gas-holder. Where very pure hydrogen is required, a purging can be interposed.

5663. In another type of furnace Messerschmitt makes use of apparatus as shown in Fig. 152. The reaction is carried out at different planes in this furnace. The walls are provided at different heights with heating channels *cc*. The gas and air nozzles 1, 2, 3 and 4 are so disposed that the heating gases are discharged tangentially into the furnace in such a man-

mer as to prevent local overheating of the iron. The oxidized iron in the different zones of the furnace is successively reduced and heated and the waste gases from one zone are burned by

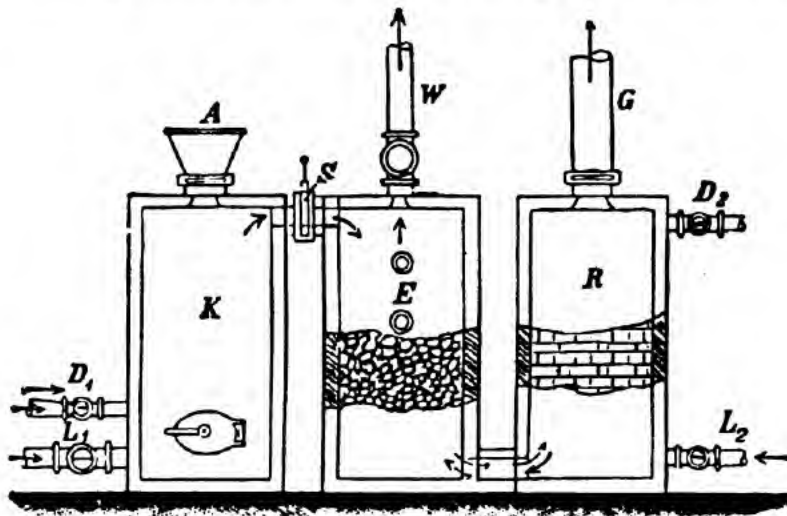


FIG. 153.

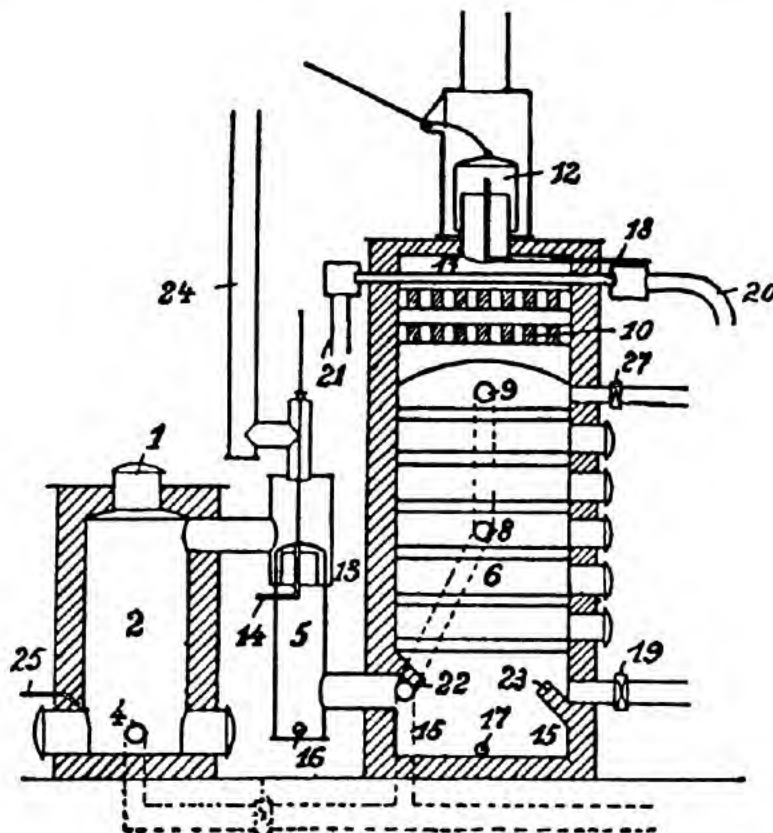


FIG. 154.

the aid of a blast of air in a higher zone. In the upper part of the structure the checkerwork *g* enables preheating of the reducing gas and steam.

5664. In Fig. 153 is shown a hydrogen-generating apparatus designed by Strache.³⁸ *K* is a gas producer, the gas from which passes through the reaction chamber *E*, containing iron filings, and is burned in the checkerwork *R*. On passing steam through the checkerwork in a reverse direction the steam becomes superheated and when brought into contact with the iron filings in *E* hydrogen is produced and is withdrawn at *W*. Another apparatus designed by Strache³⁹ is shown in Fig. 154. The water-gas generator 2, provided with inlets 25 and 4, for steam and air respectively, is connected with the reaction chamber 6, by the pipe 5, provided with a gas-discharge pipe 24. Just above the place where the pipe 5 enters the reaction chamber is a baffle 22, and on the opposite side of the chamber is a similar baffle 23. A branch from the air-supply pipe opens just below the baffle 22, and similar branches open at 8 and 9. The reaction chamber 6 is divided into compartments by gratings on which the iron reaction material is placed. In the upper part of the chamber, above a regenerator 10, are purifying retorts 11, the gas to be purified entering by 20 and the purified product leaving by 21. When the apparatus has been brought to the proper temperature and is ready for the production of hydrogen, steam is introduced through the pipe 14, below the valve 13, so as to displace any gases from the pipe 5 and the ash-pit 15. Steam is then introduced through the tube 18, below the valve 12, displacing gas from the reaction chamber from the top downwards. The hydrogen produced passes away through 19 to a holder, from which it may be passed through the pipe 20 into the purifying retorts 11, charged with potash lime.

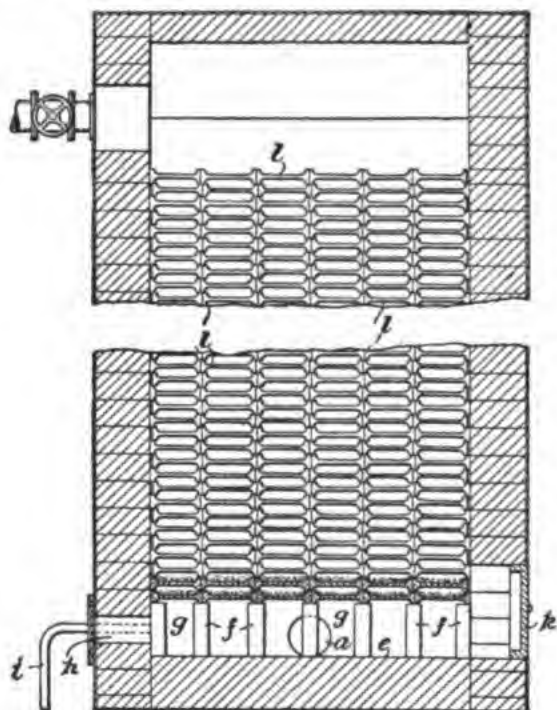


FIG. 155.

up in the furnace, they form a number of narrow flues containing a shallow layer of iron and running in a zigzag course from bottom to top of the furnace and affording free passage for the steam or reducing gas. These narrow flues, so to speak, divide up the mass of refractory material into a cellular structure such that the gases can pass freely through the cell flues over the iron.

5666. An apparatus employed by the Internationale Wasserstoff-Aktien-Gesellschaft is shown in Fig. 156. On the left is a gas producer supplying fuel gas to heat the two vertical retorts shown on the right. The heating gases and products of combustion move in the direction indicated by the arrows and finally pass to an exit flue. The valves *a* and *b* are opened and water-gas flows through the iron ore filling the retorts, reducing iron oxide to finely divided metallic iron. When reduction has sufficiently progressed the valves *a* and *b* are

5665. Elworthy⁴⁰ places the iron in a large number of separate trays of refractory firebrick or the like, each adapted to contain a shallow layer of iron in finely divided form and to be built up in successive layers from bottom to top of the furnace, so as to form a close-lying refractory filling (Fig. 155). The trays are open at their ends to enable the steam or gas to pass freely over them in contact with the iron when built up, and they have supporting flanges for supporting the under face of one tray at a suitable distance from the material on the tray below, and this under face of the tray radiates a quantity of heat onto the shallow layer of metallic iron during the heat-absorbing or oxidizing stage, while at the same time superheating the steam as it passes along the narrow shallow channel between the upper and lower series of trays. When the trays are built

³⁸ Brahmer, *Chemie der Gase*, 91.

³⁹ Ger. Pat. 253,705, Oct. 26, 1910.

⁴⁰ U. S. Pat. 778,182, Dec. 20, 1904.

closed and the three-way valve *c* is opened. Steam is admitted by the valve *d* and hydrogen is withdrawn at *e*. When the iron becomes reoxidized the steam is shut off and the oxide again reduced by water-gas. The reducing gases after passage through the retorts are burned in the combustion chamber. The hydrogen exhibits a purity approaching 98 per cent at a cost of 4 cents per cubic meter.⁴¹

5667. Schaefer⁴² produces hydrogen from steam in an apparatus which consists of a core of coarse material such as iron bars, stones, etc., while the outer portion of the contact sub-

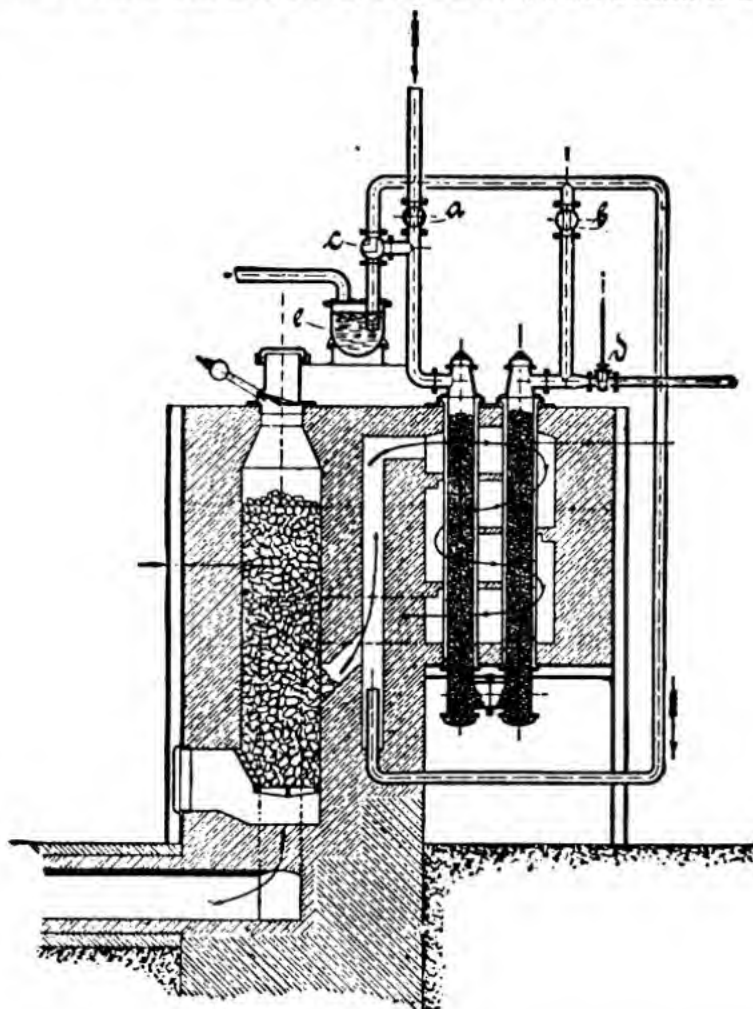


FIG. 156.

stance consists of finer pieces of iron. It is claimed that by this method a more equal distribution of heat is obtained than would be were all the particles of the same size.

Figure 157 is a view of the hydrogen generator, *b* and *b*₁ being the coarse and fine iron material respectively. A layer of stones, *a* and *a*₁, is placed at the top and bottom better to utilize the heat generated and to give an advantageous control over the reactions which take place.

⁴¹ *Chemie der Gase*, Brahmer, Frankfort, 1911, 93.

⁴² U. S. Pat. 1,144,730, June 29, 1915; Brit. Pat. 16,140, 1914; *Chem. Abst.*, 1926, 98; Ger. Pat. 291,022, July 15, 1913; *J.S.C.I.*, 1915, 824; *Chem. Abst.*, 1917, 873. Cf. U. S. Pat. 1,172,908, Feb. 22, 1916.

5668. Rogers uses a cast-iron retort which is rectangular in cross-section, having one side longer than the other; the gases are caused to flow through the retort in a direction transverse to its longer axis.⁴³

5669. Rochet ⁴⁴ constructs and works an apparatus with a view to regulate the temperature during the reduction phase within limits which will prevent deposit of carbon either from carbon monoxide (low temperature) or from hydrocarbons (high temperature). This he effects by placing the reacting mass in an annular compartment between two cylindrical vessels through which heating gases flow continuously, in a circuit independent of that of the reducing gases.

5670. The apparatus and processes sponsored by L'Oxyhydrique Française are intended to make the steam-iron method of hydrogen manufacture more economical. In the iron-steam process the regeneration of the metal is effected by reducing gases produced in blast furnaces, gas works, coke-ovens, metallurgical plant and like installations, the reducing gases being pref-

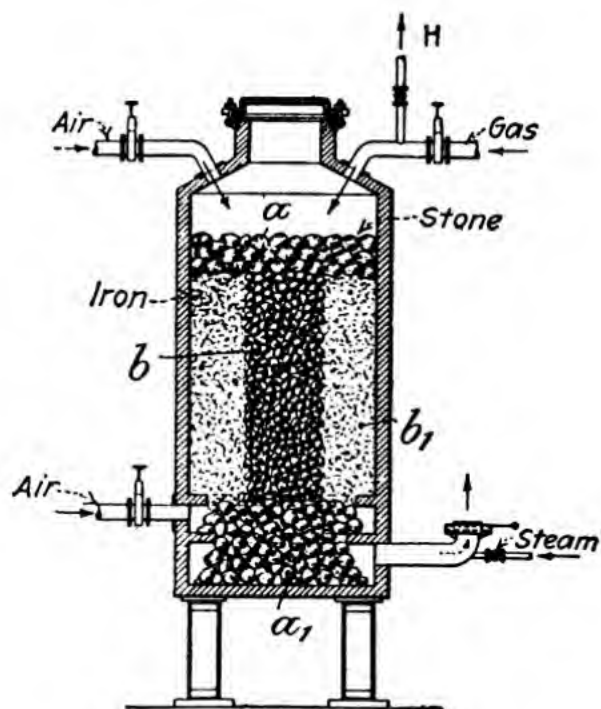


FIG. 157.

erably used in excess and preheated by waste gases. When coke-oven gases are employed for the reduction they are heated by passing them through brick heat recuperators in which the reducing apparatus is situated. Burnt gases, after heating the ovens, pass through the iron oxide and finally give up their heat to the usual brick piles of the recuperators. The coke-oven gas preheated in the recuperators passes on to the reducing apparatus containing the hot iron oxide, the issuing gas containing the excess reducing gases being employed in any part of the plant. In a second example coal gas is used for the reduction after the recovery of by-products and desulphurization, and the coal gas is preheated in the dampers in which the drawn coke is extinguished. In a third example the reducing gas is produced independently of the furnace plant, and is preheated by waste heat.⁴⁵

⁴³ Brit. Pat. 251,124, May 29, 1925, to Rogers.

⁴⁴ U. S. Pat. 1,617,965, Feb. 15, 1927.

⁴⁵ Brit. Pat. 206,822, Oct. 17, 1923, to L'Oxyhydrique Française; *Chem. Abst.*, 1924, 1183. Cf. Ger. Pat. 433,519, Mar. 3, 1925; *Brit. Chem. Abst.*, 1927, 482B.

5671. Hydrogen-Producing Apparatus.⁴⁶ Steam is passed through a number of cylindrical chambers, constructed of refractory brickwork, and containing metal oxides of a reducing character; the chambers may be lined with sheet iron. The outlets of the chambers are connected to branch collecting pipes and are provided with throttles for the regulation of the gas flow through each individual chamber.

5672. Parsons⁴⁷ describes a substantial modification of the usual process. Pyrophoric iron, produced by the action of producer gas on ferrous oxide below 600°, is treated with steam (below 700° to prevent the formation of magnetic iron oxide); the hydrogen is recovered and the ferrous oxide produced is used again in the process.

5672A. According to another proposal steam is passed through carbon raised electrically to incandescence, and hydrogen is obtained from the water-gas produced by removal of the carbon dioxide, etc. Alternatively, the water-gas is employed to reduce ferric oxide and, after removal of the excess steam and carbon dioxide, is repassed through the incandescent carbon together with the requisite quantity of steam; the reduced iron is used to decompose further quantities of steam, the first, impure hydrogen thus obtained being added to the circulating reducing gas and the pure hydrogen subsequently obtained being used for the preparation of ammonia.^{47a}

5672B. Hydrogen is prepared by decomposition of steam by metallic iron; the metallic iron is regenerated by coke-oven gases or other gases containing hydrogen and methane; to furnish the amount of heat necessary to operate this reduction a part of the gas is burnt with air or oxygen.^{47b}

5672C. A device is described for varying the flow of steam in the production of hydrogen by passing steam over iron.^{47c}

5673. Michalski⁴⁸ describes a process which is not easy to classify. Carbon (coke) is completely oxidized to carbon monoxide by molten ferrous oxide, produced by the action of oxygen on molten iron. Hydrogen may be generated by the action of superheated steam on the metallic iron.

5674. FURTHER REFERENCES ON THE STEAM-IRON PROCESS⁴⁹

- Belou. Brit. Pat. 7518, May 25, 1887. (E).
 Bosch. U. S. Pat. 1,102,716, 1914. (E).
 Caro. Ger. Pat. 249,269, Aug. 30, 1910. (E).
 Edwin. French Pat. 612,238, Oct. 8, 1925. Waste gases of process passed through high-tension electric arc and returned to the process. *Brit. Chem. Abst.*, **1927**, 409B.
 Gautier and Clausmann. *Compt. rend.*, 1910, **151**, 355. (E).
 Gerhartz. Ger. Pat. 226,543, June 23, 1909. (E). A process using molten metal.
 Lewes. Brit. Pat. 20,752, Dec. 19, 1890. (E).
 Pintsch A.-G. French Pat. 466,739, Dec. 30, 1913; *Chem. Abst.*, 1915, 1376. (E).
 Ramage. U. S. Pat. 1,224,787, May 1, 1927. (E).
 Saubermann. Brit. Pat. 401, 1911. Addition of catalytic metals. (E).
 Spitzer. U. S. Pat. 1,118,595, Nov. 24, 1914 (E). Brit. Pat. 6,155, 1914; *Chem. Abst.*, 1914, 920 and 1915, 29.
 Taylor. *Industrial Hydrogen*, 1921, 25-59.
 Tully. Brit. Pat. 16,932, 1915; *J.S.C.I.*, **1917**, 540. (E).
 Vignon. French Pat. 373,271, Jan. 2, 1907. (E).

⁴⁶ Brit. Pat. 230,046, Feb. 17, 1925, to L'Oxyhydrique Française.

⁴⁷ U. S. Pat. 1,658,939, Feb. 14, 1928, assigned to Metal Res. Corp.; *Brit. Chem. Abst.*, **1928**, 262B. Cf., Can. Pat. 264,830, Oct. 5, 1926, to Peacock.

^{47a} Norsk Hydro-Elektrisk Kvaestof-A.S., French Pat. 627,665, Jan. 18, 1927; *Brit. Chem. Abst.*, **1930**, 312B.

^{47b} Bamag-Meguain A.-G., French Pat. 668,929, Feb. 4, 1929; *Chem. Abst.*, **1930**, 1710. See also French Pat. 669,777, Feb. 18, 1929, to the same concern.

^{47c} French Pat. 662,871, Oct. 24, 1928, to Comp. de Prod. Chim. et Electrometallurg. Alais, Froges et Camargue; *Chem. Abst.*, **1930**, 475.

⁴⁸ Brit. Pat. 226,500, Dec. 17, 1923.

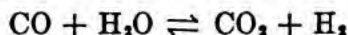
⁴⁹ In these references (E) means: Ellis, *Hydrogenation of Oils*, 2nd edition.

CHAPTER LVII

HYDROGEN (II)

THE WATER-GAS CATALYTIC PROCESS

5700. Within a certain range of temperature and in presence of suitable catalysts carbon monoxide and steam react with one another. The reaction is expressed by the equation:



The products are, therefore, a mixture of hydrogen, carbon dioxide, carbon monoxide and water vapor. If conditions are favorable for the equilibrium to tend to the right we get a gas mixture containing little monoxide and much dioxide and hydrogen. Carbon dioxide is much more easily removed from gas mixtures than is the monoxide.

5701. This reaction is the basis of a rapidly developing hydrogen process. Water-gas is passed over catalysts: the mixed gases are scrubbed with water under pressure: the residual carbon monoxide is removed by absorption and pure hydrogen (mixed in practice with nitrogen, argon, etc.) is obtained.

5702. The process was foreshadowed in an article by Hembert and Henry ¹ who passed superheated steam over coke heated to redness, whereby a mixture of hydrogen and carbon monoxide was formed. This mixture was led into a second retort filled with refractory material, also heated to redness. In the second retort steam was allowed to enter heated to its point of dissociation. The gases acted upon one another, hydrogen and carbon dioxide being formed. The carbon dioxide was absorbed by milk of lime. In this way 3200 cu. m. hydrogen are said to have been obtained from 1 ton of coke.

5703. One of the earliest descriptions is that by Naher and Müller who prepared water-gas by blowing superheated steam into a generator filled with coke, which had been heated to about 1000° C., and exhausted, and passed the gas produced, mixed with superheated steam, over a contact mass of rhodium- or palladium-asbestos at 800° C. The resulting hydrogen then was freed from the accompanying carbon dioxide.²

5704. Buchanan and Maxted ³ prepare hydrogen by passing a mixture of carbon monoxide or gases containing carbon monoxide and steam over a catalyst consisting of an alkali ferrite which has been lixiviated so that a portion of the alkali is removed; the alkali ferrite may be prepared by roasting ferric oxide,

¹ *Compt. rend.*, 1885, **101**, 797.

² Ger. Pat. 237,283 of 1910.

³ Brit. Pat. 6,476, Mar. 14, 1914; *J.S.C.I.*, 1915, 177; *Chem. Abst.*, 1915, 2434.

from burnt pyrites, with sodium carbonate. Another method of producing hydrogen due to Buchanan and Maxted⁴ depends on the interaction of carbon monoxide and steam in the presence of a catalyst consisting of or containing a metallic couple; iron-copper or iron-silver couples are suitable. The catalyst may be made from lixiviated alkali ferrite, by reducing the ferric oxide therein to the metallic state by hydrogen, moistening with a solution of copper nitrate, and finally heating, preferably in a current of reducing gas, or washing, to remove nitrates. Gases containing carbon monoxide may be used instead of carbon monoxide in a state of purity. The couple is heated to 500° C. while passing carbon monoxide and an excess of air over it.

5705. The catalytic process for the manufacture of hydrogen has acquired great importance because of the immense quantity of hydrogen made by it for ammonia synthesis. As worked for this purpose it is known as the B. A. M. A.-G. and, in the Bosch modification, is the sole source of hydrogen now used by the Badische Company for ammonia synthesis. This particular process uses as "raw material" a mixture of water-gas and producer-gas and furnishes a mixture of hydrogen and nitrogen in the ammonia proportions.

5706. The reason for using producer-gas in the Bosch process, instead of the simpler method of admitting air to the water-gas generator during the "making" stage, is economy. Producer-gas can be made from fuel of a much lower grade than can be used for making water-gas. For other hydrogenations the gas for the catalytic process must be water-gas. Even with this there is some nitrogen and this gas will accumulate during the cycle of operations.⁵

5707. The water-gas is carried with excess of steam, through converters, at 400°–600° C., over catalysts. Excess of steam is favorable for conversion. At 400° C., with 3 volumes of steam per unit volume of gas the equilibrium mixture contains 0.45 per cent of carbon monoxide: with 5 volumes of steam it contains 0.26 per cent. The converters are carefully lagged and with efficient heat conservation the reaction heat will maintain the necessary temperature. A little air is occasionally admitted if there is a loss of heat causing a fall of temperature. In practice about 90 per cent conversion is attained.

5708. Patart has devised a vertical column heat exchange and water recovery apparatus for economical working of the catalytic water-gas process.⁶ Grossmann^{7a} describes a hydrogen producer for intermittent working of contact chambers.

⁴ Brit. Pat. 6,477, Mar. 14, 1914; *Chem. Abst.*, 1915, 2434; *J.S.C.I.*, 1915, 552.

⁵ The principal Badische Co. patents covering this process and its modifications are: U. S. Pats. 1,113,096, Oct. 6, 1914, 1,113,097, same date, 1,115,776, Nov. 3, 1914, to Bosch and Wild; French Pat. 459,918, July 2, 1913, to Badische Co.; Austrian Pat. 72,430, Sept. 11, 1916, to Badische Co.; French Pat. 463,114 of 1913; Ger. Pat. 297,258, Sept. 11, 1914 (addition to Ger. Pat. 292,615); Ger. Pat. 282,849, 1913; Ger. Pats. 292,615, 1912, and 293,943, 1913, all to the Badische Co.; U. S. Pats. 1,157,689 of 1915, and 1,200,805 of 1916, to Bosch and Wild; Ger. Pat. 279,582 of 1913, and Brit. Pats. 27,117 of 1912, 27,963 of 1913, to Badische Co.; Swiss Pat. 71,803 of 1916; Norwegian Pat. 26,689 of 1916; Ger. Pat. 284,176 of 1914, to Badische Co.; Brit. Pat. 12,978 of 1913, to Badische Co. and U. S. Pat. 1,128,804 to Mittasch and Schneider.

⁶ Brit. Pat. 228,153, Jan. 21, 1924.

^{7a} Ger. Pat. 458,187, July 9, 1926; *Brit. Chem. Abst.*, 1930, 283B.

5708A. In the production of hydrogen from water-gas, the reaction tubes are surrounded at the lower ends by water jackets and at the upper ends by a jacket through which water-gas circulates. The hot reaction gases vaporize the water and carry steam with them.⁵⁶

5709. Catalysts for the Water-gas Process. According to the Badische Co.'s own published descriptions and those furnished by Bosch, Wild, Mittasch and Schneider the catalysts used are of the most varied types. But it is believed that, in practice, an iron oxide catalyst with a promoter, such as a chromate, is in almost exclusive use. However, we will give the published descriptions.

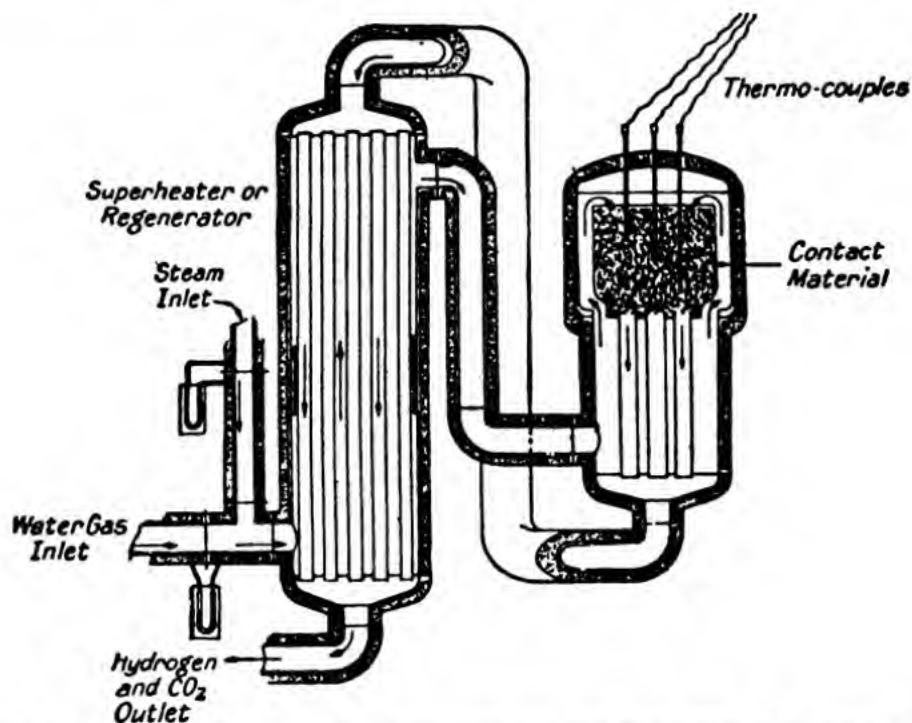


FIG. 158.—DIAGRAM OF BADISCHE CO. CONVERTER FOR THE CATALYTIC WATER-GAS PROCESS.

5710. Bosch and Wild produce hydrogen by passing carbon monoxide and steam over a catalytic material consisting of nickel or cobalt or non-metallic refractory material, which may be molded into porous blocks. Iron may be substituted for nickel and cobalt provided it is supported on an inert substance. Bosch and Wild have found that it is possible to carry out the reaction to good advantage by passing carbon monoxide and steam over a form of catalytic agent containing at least 30 per cent of finely divided nickel and more than 70 per cent of non-metallic, indifferent, refractory and porous material, the catalytic agent being porous and shaped into the form of blocks, tubes, rods, or the like. It is stated that excellent results can be obtained by preparing an oxide, hydroxide or

⁵⁶ Brit. Pat. 324,158, Nov. 19, 1928, to I. G.; *Chem. Age* (London), 1930, 308; *Brit. Chem. Abst.*, 1930, 268B.

carbonate of nickel, either by precipitation from solutions of its salts, or by heating suitable salts, such for instance as the oxalate or nitrate, while avoiding too high a temperature, then molding the resulting products and if necessary heating before introduction into the reaction furnace. The action of the catalytic agent is very satisfactory at temperatures of about from 400° to 500° C., or even less down to 350° C., but temperatures above 650° C. should be avoided. It is advisable to keep both the catalytic agent and the gases free from substances such as sulphur and chlorine which have a deleterious action. The following illustrates the method of producing a catalytic agent and of producing hydrogen by its means. Prepare a nickel hydroxide paste by introducing 5 parts of 25 per cent milk of lime into 7 parts of molten nickel nitrate, add 10 parts of precipitated green nickel oxide (NiO), knead the whole well, mold into the shape of briquets and heat up to 500° C. Then place the briquets in a suitable furnace and pass through it a mixture of pure carbon monoxide with an excess of steam, while maintaining a temperature of about 500° C.

5711. A catalyzer containing cobalt is prepared as follows:

Mix together 10 parts of finely divided cobalt oxide (prepared by raising cobalt nitrate to a red heat), 1 part of calcined magnesia, and 2 parts by volume of a 50 per cent magnesium nitrate solution. Press the mixture into small briquets, dry and heat up to 500° C.

When using an iron catalyzer, the following formulas are recommended:

(1) Add a solution of 100 parts of calcined sodium carbonate in 500 parts of water to a solution of 250 parts of ferrous sulphate in 500 parts of water. Filter off the precipitate and wash it, and then, without drying, mix it with 5 parts of slaked lime and dry until a paste is obtained which is then kneaded, rolled out, cut into cubes, dried, and heated at about 500° C. Instead of slaked lime, an agent can be employed which decomposes upon being heated, such for instance as 14 parts of calcium nitrate, or a mixture of 14 parts of calcium nitrate and 6 parts of ammonium nitrate.

(2) Knead to a paste 10 parts of finely divided iron oxide, such, for instance, as the crocus martis of commerce, and a solution of 4 parts of aluminum nitrate in 4 parts of water. Form this paste into pieces of the desired shape, which then dry and heat at 400° C. in a current of air. In this example, the aluminum nitrate solution can be replaced by, for instance, a solution of 3.5 parts of magnesium nitrate in 3.5 parts of water.

(3) Melt 40 parts of crystallized ferric nitrate at from 50° to 60° C. and stir in a mixture of 5 parts of caustic lime, 15 parts of water and 2 parts of caustic potash. Then mix this product with 50 parts of precipitate which has been obtained according to (1) and then dried, work the mixture in a kneading machine until a plastic mass is obtained, roll this out, cut it into cubes, dry it and heat at 500° C. Sometimes it is desirable to pass over it a current of air or of carbon dioxide.

(4) Heat and stir ferric nitrate at 180° C. until its nitric acid is almost completely driven off, pass the residue through the finest sieve and mix 10 parts of this with 1 part of calcined magnesia, moistening it with a solution of 1 part of

potassium carbonate in 1.6 parts of water. Press the mass into briquets, dry them and heat to about 600° C.

(5) Boil 2.5 parts of wheat starch with 15 parts of water until a stiff paste is obtained, stir in 1 part of potassium carbonate, add 20 parts of iron oxide obtained by carefully heating iron oxalate to a temperature not exceeding 600° C. Knead the whole until a plastic mass is obtained, form it into briquets, dry it and heat at about 600° C. In this example, gum tragacanth, dextrin, or gum arabic, can be employed instead of the starch.

(6) Mix 9 parts of ferric oxide hydrate with 1 part or more, of ferric oxalate and then work up the mixture to a paste with a solution of 2.5 parts of calcium nitrate in 2 parts of water. Press the paste into suitable shapes and dry slowly in a current of air at about 500° C. Then pass a mixture of pure carbon monoxide with an excess of steam over the catalytic agent thus obtained, while maintaining a temperature of about 500° C.

(7) Pass a current of carbon monoxide mixed with steam over iron in a state of fine division which has been preferably molded in a briquet press, at the same time gradually heating the catalytic agent, but avoiding temperatures above 600° C.

(8) Mix ferric oxide hydrate with sufficient concentrated calcium nitrate solution to obtain a paste of suitable consistency, then bring this paste into suitable shapes and dry it in the contact furnace while gradually raising the temperature to about 500° C. Then pass a mixture of carbon monoxide and steam over the catalytic agent, while avoiding temperatures above 600° C. Even if the gases are passed rapidly through the reaction furnace, an almost complete conversion of the carbon monoxide into carbon dioxide takes place.

(9) Heat ferric nitrate to about 200° C. so as to convert it into oxide. Moisten the latter with aluminum nitrate solution and then mold it into suitable shapes and heat it at about 400° C., until the nitrous gases are driven off. Then place the catalytic agent in the contact furnace and pass a mixture of carbon monoxide and steam through the furnace while avoiding temperatures above 600° C.

5712. Contact masses prepared by saturating pumice with a solution of nickel or cobalt chloride and subsequently igniting, are stated by the Badische Co. not to be satisfactory in the production of hydrogen from carbon monoxide and steam. Good yields of hydrogen are obtained, however, by using contact masses prepared by impregnating suitable materials with relatively small quantities of solutions of nickel salts free from halogens and sulphur.

5713. In addition, the Badische Co. say that suitable catalytic mixtures consist of iron, nickel, or cobalt or their oxides, mixed with oxygen compounds of chromium, thorium, uranium, beryllium, or antimony; iron mixed with less than its weight of nickel; iron oxide of low activity coated with finely divided iron oxide prepared at a low temperature, or zinc, lead, copper, vanadium, manganese or titanium, together with a promoter. The contact masses may be in the form of powder, porous lumps, etc., and binders, carriers, etc., may be added. The presence of chlorine, phosphorus, bromine, or silica in the catalytic mixture should be avoided. The following examples of the preparation of the catalytic

mixtures are given: A mixed solution of ferric and chromium nitrates, with or without aluminum nitrate, is precipitated by ammonia and the hydroxides are filtered off and pressed into suitable shapes; a mixture of ferric nitrate, ammonium chromate, and thorium nitrate, is heated to give the oxides; a solution of ferric nitrate, nickel nitrate, and chromium nitrate is precipitated by potassium carbonate and the precipitate filtered, washed, shaped, and dried; fine meshed wire netting is treated with ferric nitrate solution, and heated to decompose the nitrates; chromium nitrate or acetate is precipitated by ammonia, the hydroxide is mixed with precipitated zinc oxide, shaped and dried; beryllium oxide may also be used; a mixture of lead nitrate or lead acetate and uranium nitrate solution is precipitated with ammonia, the precipitate is filtered, made into lumps, and heated; copper and zirconium nitrate solution is precipitated by sodium carbonate or potassium carbonate, filtered, the alkali salt washed out partly or completely, and the product molded and dried; mixtures of oxides of manganese and chromium, titanium and antimony, vanadium and chromium or chromium and thorium are also suitable; aluminum oxide, alkali carbonates, etc., may be added as binding agents or promoters; a solution containing cerium and chromium nitrates is precipitated with ammonia, the precipitate filtered off, partly dried, made into a paste, shaped, and dried; other rare-earth salts may replace the cerium nitrate.

5714. The Badische Company also employ as catalyst, spathic iron ore, or a hydroxide iron ore, which has not at any stage of the process been subjected to a temperature appreciably higher than 650°. The catalyst may be employed in the form of grains, or may be made into shaped pieces with the aid of binding agents, such as hydroxides or salts of iron, aluminum, etc. The presence of phosphorus, sulphur or silica is objectionable.

5715. Evans and Newton ⁷ undertook to determine the activity and robustness of certain catalysts for the catalytic water-gas hydrogen process. For details of their method (small scale laboratory) the original must be consulted. What they sought, of course, was a catalyst, robust and cheap, sufficiently active to catalyze the reaction at a temperature (380°–444° C.) favorable in equilibrium conditions. Of all those they tried, catalysts containing cobalt oxide, pure or promoted and supported, were the most active. Unfortunately the cobalt catalyst is short-lived in presence of even small quantities of sulphur compounds in the gas. On the whole, for ordinary working conditions, iron catalysts seemed most satisfactory. Of these a mixture of artificial hydrated magnetite with alumina (2–5 per cent) and potassium oxide (1 per cent) was the best. It is reduced in activity by presence of sulphur compounds, but attains a constant activity even in these conditions, and can be restored to full activity by passage over it of pure water-gas.

5716. Another triple catalyst material containing iron and potassium oxides, with manganese oxide, is proposed by Heissler.⁸ For the catalytic steam water-gas hydrogen process at 500°–600° C., Heissler prepares a catalyst by heating to

⁷ *Ind. Eng. Chem.*, 1926, **18**, 513.

⁸ U. S. Pat. 1,672,528, June 5, 1928.

approximately 800° C. a mixture containing iron as its major ingredient and potassium and manganese as minor ingredients.

5717. According to Bray and Doss ⁹ certain samples of dry manganese and copper oxides when ground together form a catalyst which is much more efficient in the catalytic oxidation of carbon monoxide than the constituent oxides. No change in efficiency occurs when the granules of mixed oxides are powdered, but powdered single oxides are less efficient than the granules.

5718. Gülker ¹⁰ combines the catalyst mass with material capable of absorbing the carbon dioxide formed (such as an alkaline earth oxide). His object is, probably, to improve the equilibrium conditions. A mixture of water-gas with a slight excess of steam over that required to convert the carbon monoxide into dioxide is passed over a heated mixture, in granular form, of a catalyst and a substance capable of combining with the carbon dioxide produced. The catalytic mass is regenerated by heating in a current of air. Spathic iron ore may be used as catalyst. See following paragraph.

5718A. The absorbent and catalytic material for the absorption of carbon dioxide from gas mixtures comprises approximately equimolecular proportions of calcium and magnesium oxides, obtained by calcining dolomite.^{10a}

5719. Lazier ¹¹ has catalysts for the catalytic water-gas process obtained by heating to decomposition a double chromate of a nitrogenous base and zinc, copper, cadmium, magnesium, manganese, silver or iron. The mass is leached with dilute acetic acid. Examples are: catalysts made from basic zinc ammonium chromate, zinc dichromate tetrapyrindine and manganese ammonium chromate.

5720. Dominik ¹² prescribes a catalyst for the water-gas process which is based on the equation: $3\text{FeCO}_2 + \text{HNO}_2 + 4\text{H}_2\text{O} = 3\text{Fe}(\text{OH})_2 + \text{NO} + 3\text{CO}_2$. The activity of this catalyst is maintained at 390° with a water-gas containing CO_2 - 7.5, CO - 17 and H - 55 per cent. Dominik lays down that those metals only whose sulphide is readily hydrolyzed by water vapor can act permanently as activators in presence of sulphur compounds. Thus, the iron catalyst can be activated with chromium or aluminum, but not with cobalt or manganese.

5721. Dominik ¹³ has also elaborated an equation to express the activity of a catalyst for the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. Where b is the catalytic activity: $b = V/[(K - 1)(x_1 - x_2)] \times \log_e[(x - x_2)/(x - x_1)][(x_0 - x_1)/(x_0 - x_2)]$, with b constant for a given temperature and size of grain of the given catalyst, K is the velocity coefficient of the above reaction, V the velocity of flow of the reaction mixture in cubic centimeters per hour per gram of catalyst, x and x_0 are the partial pressures of carbon dioxide respectively during and before

⁹ *J. Amer. Chem. Soc.*, 1926, **48**, 2060; *Brit. Chem. Abst.*, 1927, 917A.

¹⁰ Ger. Pat. 446,488, July 31, 1926; *Brit. Chem. Abst.*, 1928, 816B; Brit. Pat. 275,273, July 30, 1926; French Pat. 647,257, July 20, 1927.

^{10a} Gülker, Brit. Pat. 301,499, Nov. 21, 1928; *Brit. Chem. Abst.*, 1930, 418B. Cf. para. 5723.

¹¹ Brit. application 301,806, convention date June 12, 1926, assigned to Du Pont de Nemours Co.; *Chem. Age* (London), 1929, 130.

¹² *Przemysl Chem.*, 1927, **11**, 557; *Chem. Abst.*, 1929, **23**, 1997.

¹³ *Przemysl Chem.*, 1928, **12**, 229.

the reaction, and x_1 and x_2 the roots of the equation $x(p_0H_2 + x - x_0)/\{p_0CO - (x - x_0)\} \{p_0H_2O - (x - x_0)\} - K = 0$. The values of b are shown experimentally to be constant for a gas mixture of the above type.¹⁴

5722. Blake's improvement¹⁵ on the water-gas catalytic process is defined negatively. It consists in the exclusion of iron group metals (iron, nickel, cobalt) from the catalyst and from the walls of the reaction vessel. This is said to reduce the tendency to carbon deposition. This exclusion is not absolute. If the walls are free from the iron group metals, the catalyst may contain a small quantity of iron: the increase of activity thereby gained compensates for the slight deposit of carbon. One catalyst mentioned consists of a dried chromium hydroxide gel. Others are: copper oxide and manganese oxide, chromium oxide and tungsten oxide, manganese oxide and vanadium oxide.

5723. Magnesia as catalyst in hydrogen production from carbon monoxide and steam is specified by Bomke.¹⁶ By the use of calcined dolomite catalyst and absorbent (for carbon dioxide) are combined.¹⁷

5724. Grenier¹⁸ uses wood charcoal in the water-gas hydrogen process, passing the gas with steam over the charcoal at 375° C.

5724A. Base-exchange bodies have been suggested as catalysts for hydrogen production.^{18a}

5725. A process, due to Humphrey, is specially intended for use when the less exigent methanol synthesis can be run in series with the ammonia synthesis. Semi-coke in lump form is made from slack coal of high caking power by carbonizing below 600° after preheating in presence of oxygen to control its caking properties. The semi-coke, which may be further heated at 800°–900° to drive off volatile matter, is fed direct from the retort to a water-gas generator operated with excess of steam and having a shallow fuel bed, and the resulting gas mixture is compressed and treated with excess of steam above 800° in the presence of a catalyst, e.g., nickel, to convert methane into carbon monoxide and hydrogen. If hydrogen for ammonia synthesis is desired the carbon monoxide is converted into carbon dioxide by treatment with steam in the presence of an iron oxide catalyst at about 500°, the carbon dioxide being removed, preferably by dissolution in water under pressure.¹⁹

5726. Similarly, Williams²⁰ passes hydrogen containing 2 to 10 per cent carbon monoxide under a pressure of 900 atmospheres at 400° over a catalyst made by heating zinc carbonate or a mixture of zinc and chromic hydroxides at 400°. In this way the carbon monoxide is converted into methyl alcohol, which is

¹⁴ *Brit. Chem. Abst.*, **1928**, 968B.

¹⁵ U. S. Pat. 1,692,811, Nov. 27, 1928, assigned to Lazote, Inc.

¹⁶ *Brit. Pat.* application 279,128.

¹⁷ *Chem. Age*, 1928, **17**, 578.

¹⁸ *Brit. Pat.* 271,523, May 23, 1927; Belgian date May 22, 1926.

^{18a} French Pat. 671,105, Mar. 8, 1929; *Chem. Abst.*, **1930**, 1946.

¹⁹ *Brit. Pat.* 282,573, Feb. 22, 1927, to Synthetic Ammonia and Nitrates, Ltd., and Humphrey and Canadian Pat. 281,814, July 17, 1928, to Humphrey (the latter assigned to Imperial Chemical Industries, Ltd.).

²⁰ *Brit. Pat.* 258,887, Sept. 23, 1926, assigned to Lazote, Inc.; *Brit. Chem. Abst.*, **1928**, 30B.

removed by cooling the gases, still under pressure, and at the same time acts as a solvent for traces of other impurities in the gases. After passing through the cooler, the last traces of water and methyl alcohol are removed by means of active charcoal, and the hydrogen-nitrogen mixture is then passed directly over the ferric oxide catalyst to obtain ammonia.

5727. Williams ²¹ also prescribes a catalyst composed of briquetted chromium oxide gel over which the mixture of steam and carbon monoxide is passed at 300°–700° C.

5727A. Larson proposes a catalyst containing copper in free or chemically combined form and an oxide of zinc, tungsten, molybdenum, cerium, vanadium, manganese, uranium, chromium or magnesium.^{21a}

5728. The following description applies to the Oppau plant. The catalytic process is conducted at approximately atmospheric pressure. On leaving the converter the gas is cooled in heat interchangers whereby the incoming gas is preheated. At the same time the excess of steam is condensed. The cool gas is compressed to 25–30 atmospheres. It is now sent up through steel towers 30 feet high packed with rings. Here it meets a down-flowing stream of water injected at the top of the towers. Solution of the carbon dioxide occurs ²² and the scrubbed gas passes out.

5729. The water containing the dissolved gas gives up its compression and fall energy by being made to operate Pelton wheels: about 60 per cent of the energy used to raise and inject the water is thus recovered.

5730. The carbon dioxide is collected and used for the gypsum method of forming ammonium chloride. Other close-knit economies are effected in characteristic fashion.

5731. The gas issuing from the scrubbing towers still contains some carbon monoxide. Two methods are available for removing this: (1) removal as formate by scrubbing with hot concentrated caustic soda solution, (2) absorption by ammoniacal cuprous solution.

5732. The formate method has had many advocates and it received a thorough trial at the works of the General Chemical Company at Sheffield, Alabama, but was abandoned because of difficulties due to precipitation of sodium carbonate.

5733. The Badische Company remove the greater part of the residual monoxide with ammoniacal cuprous formate solution and take out the last traces by treatment with 25 per cent caustic solution at 200° C. The gas from the scrubbers is compressed to 200 atmospheres and scrubbed with cuprous formate in steel towers filled with balls. Finally it passes through a similar series of towers where it is treated with the caustic soda.

5734. The ammoniacal cuprous formate solution when exhausted is deprived of its carbon monoxide by heating at slightly diminished pressure.

²¹ Can. Pat. 284,584, Nov. 6, 1928, assigned to The Lazote, Inc.; *Chem. Abst.*, 1929, **23**, 1225.

^{21a} Larson, Brit. Pat. 311,737, May 15, 1928; *Chem. Abst.*, 1930, 929.

²² There is also some unavoidable loss of hydrogen by solution.

5735. After removal of water the gas is now of a high degree of purity. It is, however, sometimes made to pass through a preliminary catalyst chamber to insure the removal of the last trace of catalyst poison.

5735A. Carbon is obtained as a by-product in the production of hydrogen by treating water-gas with steam. Carbon dioxide and sulphur compounds are removed by washing under pressure with water or ammonia liquor and carbon monoxide is absorbed in ammoniacal cuprous solution, from which it is obtained by releasing the pressure or heating. This is catalytically decomposed to obtain carbon.²²

5736. In Bellay's modification of the water-gas catalytic process,²³ water-gas from a gas producer is passed over baffle plates composed of fireclay and granulated charcoal on to which is projected a jet of superheated steam whereby the carbon monoxide is converted into carbon dioxide with the production of an equivalent quantity of hydrogen. The gas stream passes upwards through a tower containing milk of lime to remove carbon dioxide and dust, thence through a tube packed with soda-lime bricks heated at 800° to remove the last of the carbon monoxide. These bricks are made by slaking lime with a solution of sodium carbonate at 95°, screening out the fine material, and mixing it with lime water at 50° in a mold; after the vigorous reaction has subsided, the mass solidifies into bricks. After use in the purifier, the bricks are regenerated by heating at 850°-900° until carbon dioxide ceases to be evolved.

5737. An improved method of preparing the gas for the catalytic process is described by Casale-Sacchi. A mixture of oxygen (with or without nitrogen) and carbon dioxide is passed over coke heated to above 1000° C. and the carbon monoxide so produced is employed in the catalytic process for the manufacture of hydrogen. The resulting carbon dioxide can be reused. The advantage of this modification seems to be that catalyst poisons from the fuel are converted into easily removable compounds: thus, sulphur appears as the dioxide.²⁴

5737A. Meyer and Lichtenberger^{24a} produce hydrogen by allowing carbon monoxide to act on steam, and carbon dioxide on carbon in a bath of molten substance such as rock salt. The resulting hydrogen-carbon dioxide mixture is freed from the oxide in the usual way.

5737B. Beekley^{24b} proposes a modification of the process of producing hydrogen by the action of steam on carbon monoxide. His process comprises subjecting steam, together with a portion of the carbon monoxide with which it is ultimately to react, to the action of a heated catalyst, and thereafter subjecting the resulting gaseous mixture to one or more additional stages in which the gaseous mixture is cooled to substantially the temperature at which the reactants were first introduced to the catalyst, by the addition of carbon monoxide, and thereafter the resulting mixture is subjected to reaction in contact with a heated catalyst.

^{22a} Brit. Pat. 314,163, April 19, 1928, to Ewan and Imperial Chemical Industries, Ltd.; *Chem. Abst.*, 1930, 1188.

²³ Brit. Pat. 284,262, Jan. 19, 1928; Belgian date Jan. 26, 1927; *Brit. Chem. Abst.*, 1929, 95B. See also French Pat. 664,038, Nov. 16, 1928, to Bellay; *Chem. Abst.*, 1930, 928.

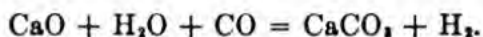
²⁴ Brit. Pat. 297,135, June 13, 1927; *Chem. Abst.*, 1929, 23, 2539.

^{24a} Ger. Pat. 478,985, Mar. 22, 1927; *Chem. Abst.*, 1930, 2254.

^{24b} U. S. Pat. 1,756,934, May 6, 1930, to Du Pont Ammonia Corp.

THE LIME PROCESS

5738. If carbon monoxide with steam is passed over lime at 500° C. calcium carbonate is formed and hydrogen is evolved.



5739. Engels ²⁵ has made a study of the reaction between carbon monoxide, water vapor and lime. The investigations show that the most suitable temperature lies between 450° to 550° C. Below 450° C. the reaction progresses too slowly, while above 550° C. the conversion does not go to completion or side reactions occur. Engels studied the effect of additions of an oxide, such as iron oxide, to the lime in order to catalyze the reaction and found its course to be much improved by the addition of a few per cent of such catalyst. The reaction is exothermic so no further external heating is necessary after the conversion has begun.

5740. In what is known as the low temperature water-gas process advantage is taken of this reaction to get hydrogen directly by acting with steam on coke in the presence of an alkali.

5741. Steam is allowed to act on carbon or carbonaceous matter to which both an alkali compound and lime have been added, the effect of the additions according to Dieffenbach and Moldenhauer ²⁶ being to lower the temperature of decomposition and to give hydrogen free from compounds of carbon and oxygen. For example, 100 kilos of charcoal or coke, impregnated with a 10 per cent solution of potassium carbonate, are mixed with 500 kilos of quicklime, and the mixture is decomposed by steam at 550° to 750° C. They also claim ²⁷ the employment of other alkali compounds—such as chlorides and sulphates—for the same purpose. The fuel is impregnated with a solution of the alkali compound and dried, or, if practical, the fuel is coked after the addition of such compound. A comparatively small amount of oxygen may be introduced along with the steam for the purpose of maintaining the required temperature inside the decomposition apparatus. Granulated coal or coke may be treated with a solution of an alkali silicate or carbonate and the mixture briquetted and subjected to the action of superheated steam at temperatures from 550° to 750° C. ²⁸

5742. Vignon ²⁹ describes a horizontal or slightly inclined rotary retort which is charged with coal, anthracite, or coke, and quicklime, and a mixture produced by the rotation of the retort. The mixture is heated to 900° to 1000° C. and water or steam passed in until the temperature falls to 700° C. The gas is withdrawn and air passed through to raise the temperature to 900° to 1000° C. and to regenerate the lime.

5743. In the process of Tessié du Motay ³⁰ water-gas mixed with steam is passed into a converter containing lime where hydrogen and calcium carbonate are formed. Figure 159 shows a plan view of the apparatus, in which A is a water-gas generator, B represents purifiers in which sulphur is removed, C designates superheaters where steam is mixed with the water-gas. The preheated

²⁵ *Über die Wasserstoffgewinnung aus Kohlenoxyd und Kalkhydrat*, Dissertation, Karlsruhe, 1911.

²⁶ Brit. Pat. 8734, Apr. 11, 1910.

²⁷ Brit. Pat. 7718, Mar. 30, 1910.

²⁸ French Pat. 417,929, Apr. 25, 1910.

²⁹ French Pat. 477,083, May 25, 1914.

³⁰ U. S. Pat. 229,338, -40, June 29, 1880.

mixture then passes to a converter shown in Fig. 160. The inclined passageways of the latter are filled with lime in contact with which the reaction

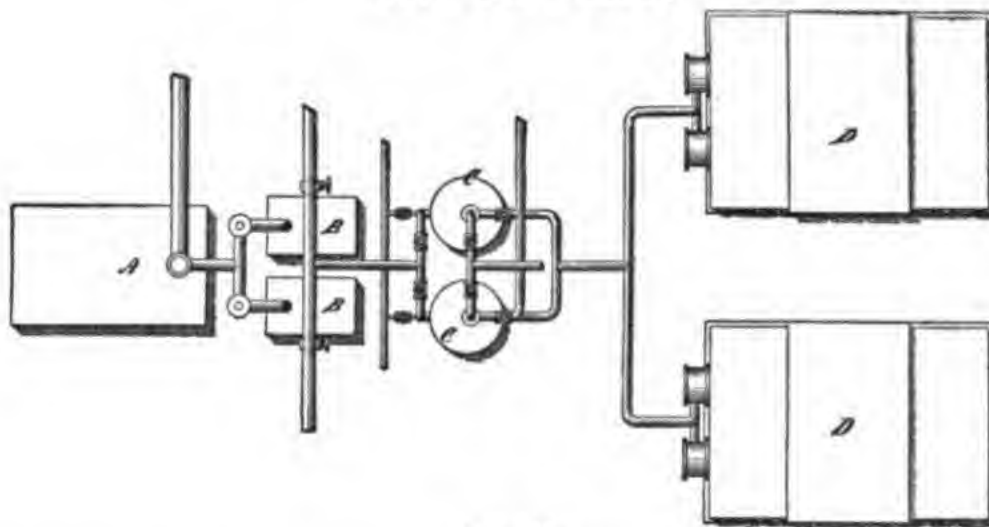
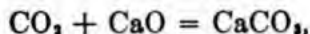
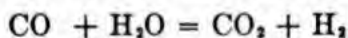


FIG. 159.

progresses, yielding hydrogen gas. In lieu of water-gas, coal gas or the vapor of naphtha may be similarly treated.

5744. The process of the Chem. Fabrik Griesheim-Elektron ²¹ involves mixing water-gas with an excess of steam and passing this mixture over lime or hydrated lime to which about 5 per cent of iron powder has been added. The lime is heated to approximately 500° C. in an upright retort fitted with an agitator.

5745. When gases containing carbon monoxide and steam are conducted over calcium hydrate or caustic soda at temperatures of 450° to 550° hydrogen is obtained. This reaction is favored materially by employing increased pressure and correspondingly increased temperatures. In the same period of time four times as much hydrogen can be secured as when operating at atmospheric pressure. Either steam or a mixture of steam and gases containing carbon monoxide is conducted over a mixture of alkali or alkaline earth and carbon, or a mixture of steam and carbon monoxide is conducted, at an increased pressure, over alkalies or alkaline earths. Pressures of 10 to 100 atmospheres and over are employed.

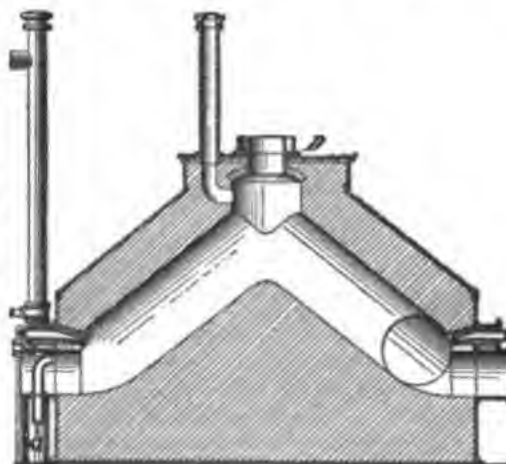


FIG. 160.

²¹ *Zeitsch. f. angew. Chem.* (1912), 2401; Brit. Pat. 2523, Feb. 2, 1909.

5746. If gases containing carbon monoxide are to be acted upon alone, good yields are secured at five atmospheres pressure. With the use of lime, a temperature of 600° to 800° is suitable, and with the use of barium hydrate and alkali, a materially lower temperature may be employed. Especial advantages are secured by conducting steam, under a pressure of ten atmospheres and more, over a mixture of lime and coal or charcoal, almost pure hydrogen being obtained. Since the thermal effect is strongly positive, generally the application of heat is not required in a sufficiently large apparatus.

5747. A tower may be used in which a charge of coal and lime is placed. The coal serves both as a source of heat and for the decomposition of steam. When by air blowing, the charge has been brought to the desired temperature, the supply of air is discontinued, and water or steam is conducted, from above, over the mixture, at twenty atmospheres pressure. The burned lime is discharged from below, mixed with fresh coal, and returned to the process. Brown coal or charcoal is preferred since they react more quickly and at lower temperatures than hard coal and coke.³²

5748. The production of hydrogen by the action of carbon monoxide and steam on quicklime is regarded by Levi and Piva³³ as dependent on the intermediate formation of calcium formate.

5749. Merz and Weith³⁴ have noted that when moist carbon monoxide is passed over soda lime heated to 300° C. or over, hydrogen is formed. A simple process for the production of hydrogen based on the observations of Merz and Weith has been put forward by the *Société générale des Nitrures in Paris*. A mixture of producer gas and water-gas is treated in the usual way to remove carbon dioxide and is then passed over hot lime, which treatment yields a mixture of nitrogen and hydrogen free from carbon monoxide. The composition of the hydrogen-nitrogen mixture may be adjusted by using different proportions of the producer gas and water-gas.³⁵

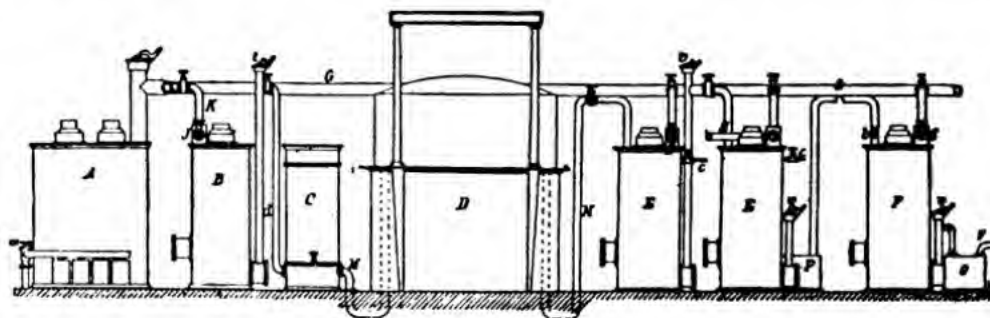


FIG. 161.

5750. Jerzmanowski³⁶ makes a hydrogen-containing gas with apparatus shown in Fig. 161. A kiln *B* filled with lime is raised to a high temperature by burning producer gas from the generator *A*. As soon as a sufficient heat is attained in *B*, an injector *H* blows into *B* steam and petroleum, which are decomposed chiefly into hydrogen and carbonic acid along with small quantities of carbonic oxide, marsh gas and other impurities. The gases pass through a cooler *C* to the gasometer *D*, and thence to purifiers.

³² Ger. Pat. 284,816, Mar. 14, 1914; Brit. Pat. 2523, Feb. 2, 1909; U. S. Pat. 989,955, 1911, to Ellenberger, assigned to Griesheim-Electron.

³³ *J.S.C.I.*, 1914, 310.

³⁴ *Ber.*, 1880, 719. See also *Ber.* 1880, 31.

³⁵ Sander, *Zeitsch. f. angew. Chemie*, 1912, 2406.

³⁶ *J.S.C.I.*, 1884, 560.

5751. The New York Oxygen Company produced hydrogen by heating together anthracite and slaked lime. On passing an excess of steam over the residue in the retorts the reverse action sets in and the slaked lime is reproduced. This sequence may be continued many times without renewing the materials.³⁷

5752. Ellis³⁸ employs a method of making hydrogen involving the treatment of lime or lime-material with carbon monoxide, or gases containing carbon monoxide. For example, carbon monoxide is passed over hydrated lime or carbon monoxide mingled with steam is contacted with lime, the latter being heated to a temperature of 450° to 600° C.

5753. The monoxide takes oxygen from the water vapor forming carbon dioxide and liberating hydrogen and the carbon dioxide combines with the lime to form calcium carbonate. This action is accelerated by the presence of catalytic material such as iron oxide and manganese oxide. The reaction is exothermic and once the mass of lime has been brought to the reacting temperature, sufficient heat is developed for continuance of the operation without the aid of externally applied heat. In fact cooling may sometimes be required as the reaction does not progress with as good yields when the temperature is much above 525° or 550° C. Another consideration is the use of an excess of steam which greatly improves the yield of hydrogen.

5754. Four to five times as much water vapor by volume as carbon monoxide should be present in order to effect substantially complete conversion. Difficulties are experienced in treating lime with gases to insure satisfactory absorption of the carbon dioxide, and it is desirable to remove the carbon dioxide as fast as it is formed in order to prevent by mass action the repression of the reaction due to the accumulation of the carbon dioxide, in the gaseous atmosphere. To carry out the conditions required for the reaction Ellis makes use of a treating apparatus comprising a series of superimposed conveyers. These conveyers are connected by chutes so that the lime and contact material, entering the uppermost conveyer, feed downwardly conveyer by conveyer and finally discharge from the lowest section.

5755. The gas or vapor mixture flows upwardly from section to section in contact with lime material which is constantly but slowly moved forward in a direction opposite to the flow of the gases or vapors and under these conditions the carbon monoxide unites with the oxygen of the water, forming carbon dioxide, which combines with the lime, thus removing the carbon dioxide, as such, from the scene of the reaction and enabling a further conversion of carbon monoxide into carbon dioxide, so that the gases discharging from the upper section of the conveyer may be practically pure hydrogen or hydrogen containing only a small measure of contaminating products.

5756. The addition of 5 per cent of iron or manganese oxide prepared by drying the precipitated hydroxide accelerates the reaction.

5757. The resulting carbonated lime is removed by a conveyer and is passed through a rotary kiln which may be heated by a producer gas or a powdered coal flame, and the lime regenerated; care being taken to not overheat the iron or manganese oxide to such an extent that its amorphous condition is lost. The regenerated lime, especially if not overheated, may be used repeatedly.

5758. In place of carbon monoxide or water-gas, producer gas, or even the vapors of oil, may be mingled with steam and passed over the lime to effect decomposition, thereby liberating hydrogen both from the oil and the water, forming first carbon monoxide and then carbon dioxide which is absorbed by the lime.

5759. In the process of Siedler and Henke,³⁹ water-gas or other gas rich in carbon monoxide is mixed with steam and the mixture passed over lumps of lime arranged in superimposed layers in a vertical tower and maintained at a temperature of 400° to 750° by heat initially supplied by the gas and by the heat of the reaction.

³⁷ *J.S.C.I.*, 1887, 92.

³⁸ U. S. Pat. 1,173,417.

³⁹ *Chem. Abst.*, 1916, 1708; U. S. Pat. 1,181,264.

HYDROGEN AS BY-PRODUCT OF PHOSPHORIC ACID MANUFACTURE

5760. When phosphate rock, consisting essentially of tri-calcium phosphate, is heated in an electric furnace with carbon and silica a slag of calcium silicate is formed and gases are given off containing carbon monoxide and elemental phosphorus. These gases may be burned to carbon dioxide and phosphorus pentoxide, and from the latter phosphoric acid may be made by hydration. But, if the phosphorus be treated with steam at about 1000°C ., or, in the presence of catalysts, at lower temperatures, it reacts with the water forming phosphorus pentoxide and liberating hydrogen.

5761. This forms the basis of an important though local and specialized method of hydrogen manufacture. The hydrogen so produced is used in the ammonia synthesis and the two end-products, ammonia and phosphoric acid, are combined in the valuable fertilizer ammonium phosphate.

5762. Liljenroth first described⁴⁰ a non-catalytic process. This necessitated an operation temperature of 1000°C ., which was not easy to maintain. At lower temperatures hydrogen phosphide was formed. But it was found that by the use of catalysts a much lower operating temperature was possible without the production of phosphine. Moreover, if phosphine was present in the gases from the electric furnace this was decomposed, the phosphorus was oxidized and the hydrogen liberated.⁴¹

5763. The process takes several forms. The temperature of reaction is obtained by the admission of air with the steam which burns some of the phosphorus. Since the hydrogen is intended for the ammonia synthesis the nitrogen so added is advantageous. The phosphorus pentoxide is condensed or is removed as phosphoric acid by hydration. The effluent gases, containing hydrogen, carbon monoxide and nitrogen can be treated in any known manner for the replacement of the carbon monoxide by hydrogen. Clearly the catalytic process (paras. 5700 to 5737) is the method of choice.

5764. In another modification the gases coming from the electric furnace are passed through a condenser which retains the phosphorus. The effluent carbon monoxide is used to preheat the charge and to raise steam. The phosphorus can be vaporized and treated with steam and air in presence of a catalyst. This produces a hydrogen-nitrogen mixture free from carbon monoxide.

5765. The catalysts specified by Liljenroth and Larsson are metals and oxides of the eighth, seventh and sixth groups, and noble and semi-noble metals of the first groups. Their list comprises: iron, nickel, cobalt, ruthenium, rhodium, palladium, osmium, iridium and platinum (eighth group); manganese (seventh group); chromium, molybdenum, tungsten and uranium (sixth group); copper, silver and gold (first group). Mixtures may be used and the catalyst may be in massive form (e.g., wire gauze), or in powder, or supported on a carrier.

⁴⁰ U. S. Pat. 1,594,372, Aug. 3, 1926 (Swedish date, Aug. 28, 1922); Ger. Pat. 406,411, Apr. 24, 1923.

⁴¹ U. S. Pats. 1,605,960, Nov. 9, 1926 and 1,673,691, June 12, 1928, to Liljenroth and Larsson (assigned to Phosphorus-Hydrogen Co.); Brit. Pat. 252,953, Sept. 22, 1925, to Liljenroth.

5766. The following is an example of the method: Pieces of pumice are soaked with a solution of equal parts of copper and nickel nitrates and are then heated to glowing temperature in a current of air. Through a chamber filled with this catalyst is led a mixture of 1 volume of phosphorus gas and 20 to 60 volumes of steam at a temperature of 550° to 700° C. The gas mixture should be supplied at such a speed that 250 liters of hydrogen are produced per hour and per gram of catalyst: in these conditions the yield is quantitative and the hydrogen produced contains mere traces of the phosphide. This catalyst is particularly robust.

5767. The catalyst may be regenerated by passing hydrogen over it at 500° to 700° C. In this way the deleterious coating is converted into a substance which, on the resumption of the steaming, is reconverted into active catalyst.⁴²

5767A. Liljenroth also proposes to make hydrogen and phosphoric acid by treating metallic phosphides, reducible by hydrogen, with water or steam at raised temperatures, oxygen being added if necessary.⁴³

5768. In 1927 at the Piesteritz works the Liljenroth process was being applied to 70 tons of phosphorus daily.⁴⁴ In the United States the process has been worked at Niagara Falls by the Phosphorus-Hydrogen Company.

5769. Modifications of the Liljenroth process have been described which differ, not in principle, but in choice of catalyst or in details of operation. Mit-tasch and Wietzel⁴⁵ use a charcoal catalyst. The same substance or, alternatively silica gel, is used to purify the hydrogen after condensation of the phosphoric acid.⁴⁶

5769A. Hydrogen may be produced by passing the vapor of phosphorus mixed with steam at a temperature of 650° C. over active carbon. The product is cooled to 110° C. to condense the phosphoric acid formed. To the mixture of steam and hydrogen derived from this step, carbon monoxide saturated with steam is added and this mixture is led over a contact agent of iron and chromium at a temperature of 550° C. The carbon dioxide which is produced is removed, leaving the hydrogen.^{46a}

5770. Urbain⁴⁷ finds that the reaction between steam and phosphorus vapor will take place at 350° C. in the presence of absorbent carbon and hydrochloric (hydrobromic or hydriodic) acid vapor. The phosphoric acid is recovered by washing the carbon, the hydrochloric acid by condensing the vapors. Alternatively the phosphorus may be absorbed by the carbon and treated with hydrochloric acid and steam.

5771. The metallic compounds of silicon, such as the silicides of copper, double silicides of copper and nickel, triple silicides of iron, copper and nickel are also used to promote the oxidation of phosphorus vapor with steam.⁴⁸

5772. Other variations are the following. In the production of phosphoric acid and hydrogen by the interaction of steam and phosphorus, the residual gases are passed into a water-cooled condenser maintained above 100° C., which thus acts as a steam generator. The gases then pass to another condenser maintained below 100° C., and low pressure steam is produced. This is compressed to raise it above atmospheric pressure, so that it may be

⁴² U. S. Pat. 1,668,539, May 1, 1928, to Larsson; Brit. Pat. 259,201, Sept. 20, 1926, to the I.-G., prescribes the addition of a small quantity of oxygen to the hydrogen used for regeneration of catalyst.

⁴³ French Pat. 595,987, Mar. 31, 1925 (convention date Apr. 15, 1924).

⁴⁴ *Chem. Age* (London), 1927, 17, 232. See also Brit. Pat. 320,598, Soc. Italiana per le Industrie Minerarie e Chimiche, Appln. date April 13, 1928, *Chem. Age* (London), 1929, 575.

⁴⁵ Ger. Pat. 431,504, Nov. 11, 1924 (assigned to the I. G.); *Brit. Chem. Abst.*, 1926, 916B. See also U. S. Pat. 1,732,373, Oct. 22, 1929; *Brit. Chem. Abst.*, 1929, 1015B.

⁴⁶ Brit. Pat. 262,455 (convention date, Dec. 3, 1925), to the I. G. Farbenind. A.-G.; *Chem. Age* (London), Feb. 12, 1927.

^{46a} I. G. Farbenind. A.-G., Ger. Pat. 480,961, Dec. 4, 1925; *Chem. Abst.*, 1929, 5016.

⁴⁷ Brit. Pat. 278,578, Dec. 6, 1926; French Pat. 638,528, Dec. 7, 1926.

⁴⁸ French Pat. 635,432, June 2, 1927, to Cie. nat. mat. colorantes et manuf. prod. chim. du nord réunies.

used again.⁴⁰ In the process just described, steam is introduced through a Körtting injector, and draws in liquid phosphorus. The mixed vapors pass over lignite coke and copper.⁴⁰

5773. Phosphorus is treated at a high temperature with a limited supply of steam, with or without the addition of air or oxygen, so that lower phosphorus oxides or acids are formed in addition to hydrogen and phosphoric acid, and oxidation to phosphoric acid is completed at a lower temperature, using air or other oxidizing agent for the purpose.⁴¹

5774. It has since been found that the oxidation can be completed simply by cooling the reaction products by addition of water or of gases or vapors free from oxygen. The oxidation is promoted by contact bodies such as copper-nickel alloys, carborundum or chamotte.⁴²

5775. Hydrogen and phosphoric acid are obtained continuously and in the pure state by treating phosphorus with water or water vapor at 300°–400° and at pressures up to 500 atmospheres. The gaseous and liquid reaction products are removed and subjected separately or together to another pressure treatment, with addition of water or water vapor if desired.⁴³

5776. Phosphoric acid and hydrogen also are obtained by treating phosphorus with water at a temperature below 600° and at a high pressure and transforming the phosphine formed in the same system or an adjoining one into phosphoric acid and hydrogen, if necessary with alteration of pressure and temperature. Catalysts such as precious metals, phosphides, phosphates or other compounds of phosphorus may be used.⁴⁴

5777. Phosphates and hydrogen are obtained when the above process is carried out in presence of ammonia or other alkalies, alkaline earths, bases, metals or salts.⁴⁵

5778. Instead of steam as the oxidizing agent carbon dioxide may be used. Phosphorus vapor and carbon dioxide are caused to interact at a high temperature, the phosphorus pentoxide formed is condensed and converted into phosphoric acid, and the carbon monoxide is mixed with steam and passed over a catalyst to obtain hydrogen and carbon dioxide for use again in the process.⁴⁶

⁴⁰ Brit. Pat. 262,447 (convention date, Dec. 3, 1925), to the I. G.; *Chem. Age* (London), Feb. 12, 1927, 167.

⁴¹ Brit. Pat. 262,454, same date, same patentee; *ibid.*

⁴² Ger. Pat. 438,178, Nov. 21, 1924; *Brit. Chem. Abst.*, **1927**, 481B.

⁴³ I. G. Farbenind. A.-G. (Wietzel, Haubach and Hüttner, inventors), Ger. Pat. 485,068, Aug. 16, 1928; addn. to 438,178; *Chem. Abst.*, **1930**, 923. See also Brit. Pat. 325,533, Nov. 16, 1928; *Chem. Age* (London), **1930**, 399.

⁴⁴ I. G. Farbenind. A.-G., Brit. Pat. 324,122, Oct. 20, 1928; *Brit. Chem. Abst.*, **1930**, 282B; *Chem. Age* (London), **1930**, 308.

⁴⁵ Bayerische Stickstoffwerke A.-G. (Ipatiev, inventor), French Pat. 670,338, Feb. 26, 1929; *Chem. Abst.*, **1930**, 1941.

⁴⁶ Caro and Frank, Brit. Pat. 308,684, March 26, 1928, to Bayerische Stickstoffwerke A.-G.; *Chem. Abst.*, **1930**, 472. See also Brit. Pats. 308,598 and -9; *Chem. Abst.*, **1930**, 471.

⁴⁷ French Pat. 624,438, Nov. 10, 1926, to Hydro-elektrisk Kvaestofaktieselskab; Norw. Pat. 45,018, Apr. 2, 1928, same patentee; *Brit. Chem. Abst.*, 1928, 927B; *Chem. Abst.*, 1928, **23**, 4210.

CHAPTER LVIII

HYDROGEN (III.)

REMOVAL OF CARBON MONOXIDE, ETC., BY LIQUEFACTION

5800. As uncarburetted or blue water-gas consists of approximately equal parts hydrogen and carbon monoxide with small amounts of other gases, much attention has been given to methods of eliminating the monoxide by solution, absorption and liquefaction. The cost of removal of the carbon monoxide by solvents such as cuprous chloride and the like appears to be too great for commercial application. As the monoxide is relatively easily liquefied by cold and pressure, while hydrogen is extremely resistant to liquefaction under like conditions, processes have been devised for removing carbon monoxide in this way. As a source of cheap hydrogen this method offers attractive possibilities to concerns requiring large amounts of the gas. For small plants the relatively high cost of installation renders the use of liquefaction processes less feasible.

5801. The pioneer work connected with the development of the liquefaction system towards a commercial goal should be credited to C. E. Tripler, who apparently was the first to devise methods and apparatus for large scale liquefaction of air and other gases. In 1893 Tripler patented ¹ the method of condensation "of a current of gas by expansion of itself over the conduit through which it passes." On this idea is based the present systems of separating hydrogen and carbon monoxide through liquefaction of the latter.

5802. The principle of liquefaction by compression with counter-current ^{1a} cooling is shown diagrammatically in Fig. 162. The reducing valve *R* is so arranged that on the side carrying the receiver *B* for the liquefied product a pressure of 20 atmospheres is maintained, while on the other side the pressure is held at 200 atmospheres. The operation is as follows. Air is drawn from *B* by the compressor *K*, passing through the outer concentric tube of the coil. After compression to 200 atmospheres the air enters the cooler *KG* where the heat generated by compression is absorbed. The cooled compressed air flows through the inner tube of the coil to the reducing valve *R* where it is released at 20 atmospheres. Circulation in this manner is kept up until the temperature is lowered to the point of liquefaction.

5803. Nitrogen boils at -193°C. , carbon monoxide at -190°C. and carbon dioxide at -78°C. while hydrogen boils at -252°C. and may easily be

¹ Brit. Pat. 4210, 1893.

^{1a} The term "counter-current" is not used here in its ordinary sense of two currents which actually meet.

retained in gaseous form at temperatures which convert the other components of water-gas to liquids or solids.²

5804. Apparatus in various forms has been devised by Linde, Claude, Hildebrandt and others for the separation of the components of mixed gases by the liquefaction of the more easily liquefied constituents. The Hildebrandt system, shown in Fig. 163, consists of a coil of pipe of relatively large diameter through which two smaller pipes extend. The latter are indicated by 1 and 7 in the upper right-hand terminus of the large coil. Gas under the requisite high pressure enters at 1, passes along one of the small pipes within the larger pipe of the large coil, emerges at 2 and passes along the central riser to the expansion chamber *E*. Expansion

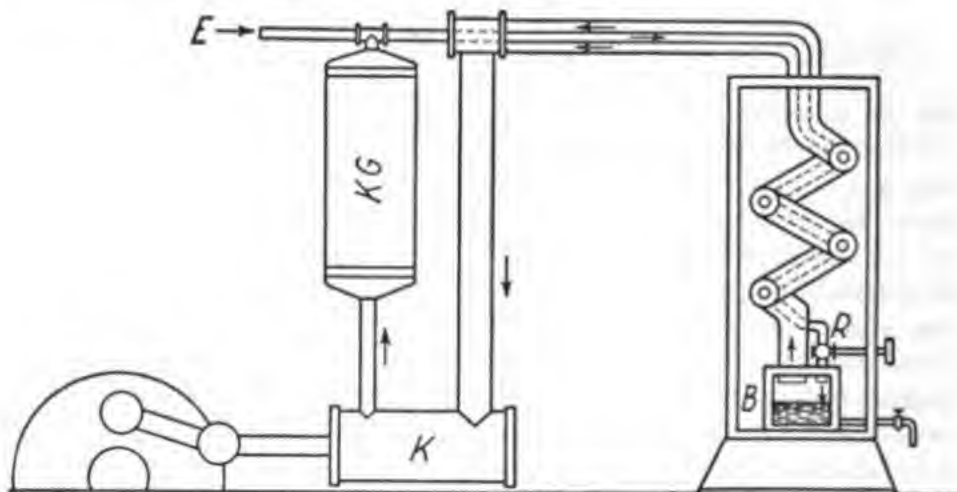


FIG. 162.

with liquefaction occurs here. The liquefied product flows through 3 into the chamber *R* and from thence into a multiple evaporating coil 4, which consists of four coiled pipes having openings along their upper sides. Evaporation of the more easily boiling constituents takes place as the product flows downwardly along the evaporating conduits. The vaporized portion departs through the perforations of the coil and passes through 5 into the large pipe *A*, moving along this pipe as a current counter to the high-pressure gas entering at 1 and passing out of the system by the horizontal pipe shown on the upper right hand. The liquid fraction collecting in *G* flows along one of the narrow pipes to 2, thence through one of the narrow pipes in the large coil, upwardly and out at 7.

5805. The Linde Processes. The Linde process, unlike the Claude process, expands the compressed gas without doing external work. Linde reports that Frank and Caro, with the aid of the Linde firm, have succeeded in the production of hydrogen of a high degree of purity from water-gas. Figures 164 and 165 show the apparatus diagrammatically.

5806. Compressed water-gas enters by the innermost tube *A*, and is cooled by expansion through the valves and return of the cooled gases by the middle and outermost tubes *G* and *E* respectively, until liquefaction of the carbon monoxide occurs; separation then takes place, the gaseous hydrogen escaping

² The production of hydrogen by liquefaction is clearly described by Linde in the Proceedings of the Third Int. Congress of Refrigeration, 1913. See also a very comprehensive treatise entitled, "Lowest Temperatures in Industry," issued by Gesellschaft für Lindes Eismaschinen, Munich.

through the valve *F* and the tube *G*, the liquid carbon monoxide passing through the valve *D* and evaporating in the middle tube. It was found impossible to liquefy the carbon monoxide, however, by the small amount of cooling by internal work of a gas containing so much hydrogen,^{2a} and the cooling was therefore aided, as indicated in Fig. 165, by cold-jacketing the lower portion of the apparatus by means of a similar apparatus producing liquid air; in this way the industrial suc-

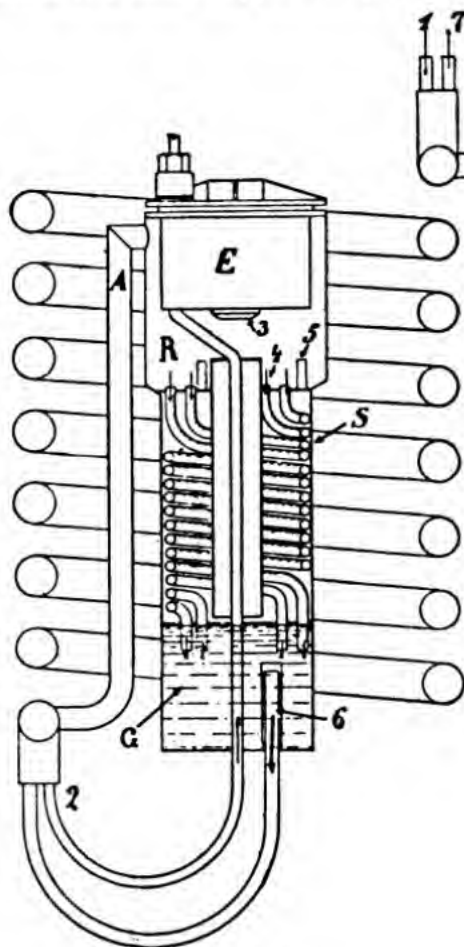


FIG. 163.

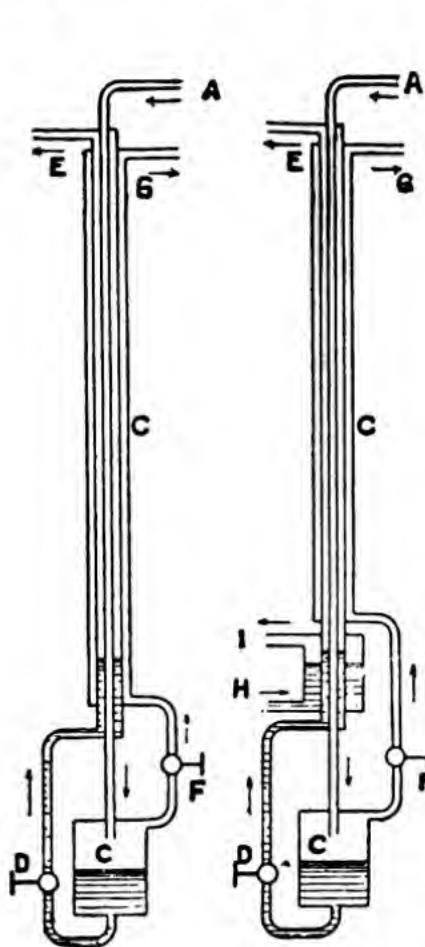


FIG. 164.

FIG. 165.

cess of the apparatus was secured, and a gas produced, containing hydrogen, 97 per cent; carbon monoxide, 2 per cent; nitrogen, 1 per cent. Removal of the carbon monoxide by calcium carbide or soda lime then yields a 99 per cent hydrogen. The gas formed from the liquid contains 85 to 90 per cent of carbon monoxide, the rest being chiefly hydrogen, and is an excellent power gas.

5807. By one process (Ges. für Linde's Eismaschinen A.-G., French Pat. 427,983, Mar. 31, 1911) the strongly cooled, compressed gaseous mixture containing hydrogen is passed

^{2a} Above -80°C . expansion ("throttling") of hydrogen causes a rise of temperature (Joule-Thomson inversion).

through a heat interchanger so as to separate it into a gaseous portion, chiefly hydrogen, and a liquid portion, consisting mainly of impurities. The mixture passes into a receiver, which is provided with two separate systems for producing expansion; the liquid portion of the mixture collects in the receiver and is expanded in the lower system, from which it passes into the interchanger in the space surrounding the tube which conveys the original mixture into the receiver, and in the opposite direction to that of the gaseous current; the gaseous portion is expanded in the upper system and passed into the interchanger in the space surrounding the tube which conveys the mixture expanding from the lower system. From the interchanger the expanded hydrogen is collected free from impurities, which are thus condensed by the cold produced by the agency of the above-mentioned expansions. A supplementary refrigerating appliance, containing liquid air or liquid nitrogen, is used in conjunction with the apparatus for the preliminary cooling of the gaseous mixture.

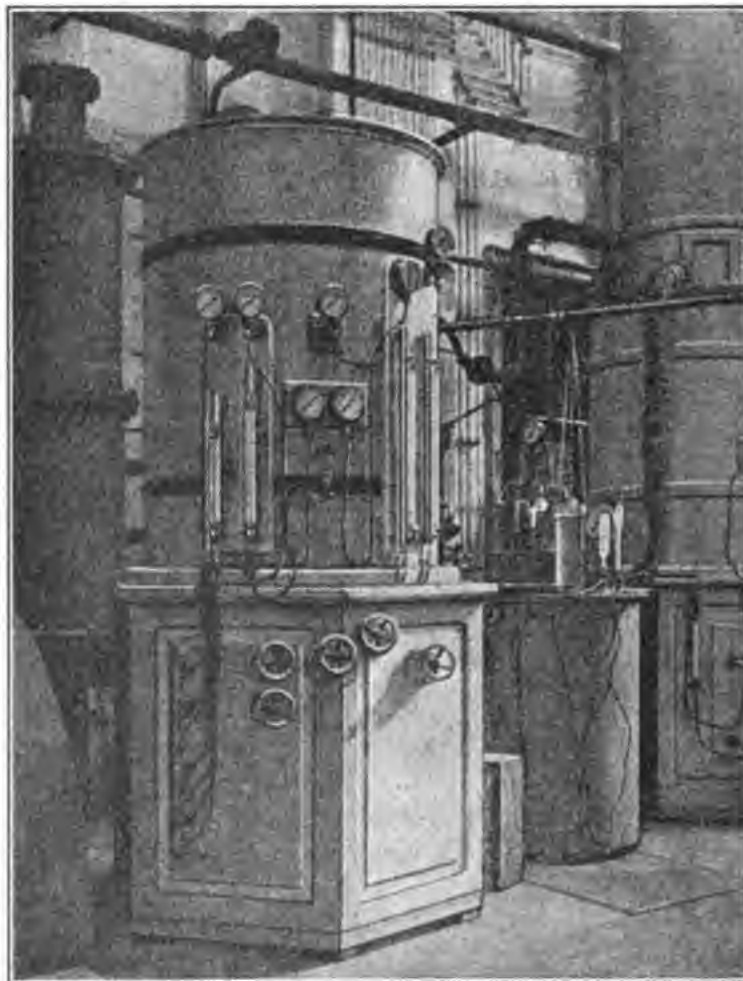


FIG. 166.—LINDE HYDROGEN APPARATUS.

5808. A modified form of the foregoing consists in removing the portion of the gaseous mixture which is not liquefied, and comprises chiefly hydrogen, without allowing it to expand, the pressure remaining equal to that to which the compressed gaseous mixture has been brought. Liquid air or liquid nitrogen, used for refrigeration, is evaporated at a pressure below that of the atmosphere, in order to obtain a more complete separation of the remaining impurities. The liquid air or liquid nitrogen is thus used only for the ultimate refrigeration of the hydrogen which has already been freed from the main quantity of condensable gases. Also, the hydrogen, before it is brought to the expansion apparatus may be subjected to slight

heating in a counter-current device, by means of the compressed gaseous mixture which has not yet been fractionated.³

5809. Frank ⁴ cools water-gas in a suitable apparatus sufficiently to liquefy the carbon monoxide and dioxide, which are then separated. If the water-gas has been produced at a low temperature, and contains chiefly carbon dioxide, with but little carbon monoxide besides hydrogen, it may be completely liquefied, and the hydrogen recovered by fractional distillation. In either case the hydrogen resulting is further purified by being conducted over calcium carbide at a temperature of over 300° C.⁵

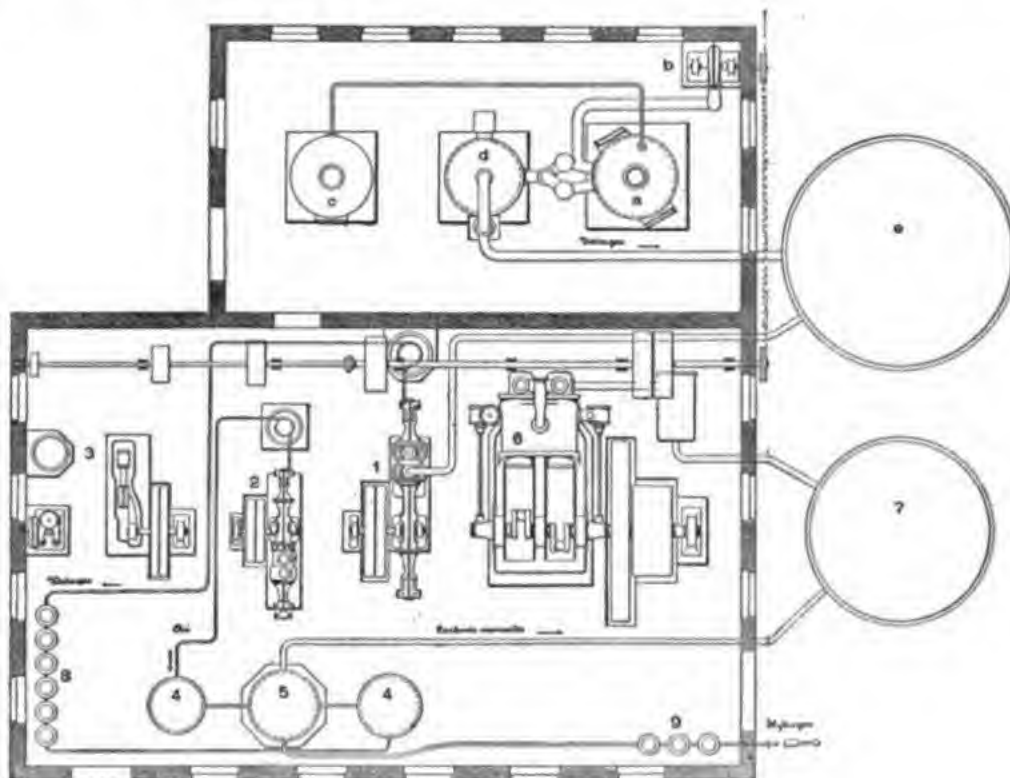


FIG. 167.

5810. The arrangement of a plant under the Linde-Frank-Caro system⁶ is shown in Fig. 167. In this illustration *a* is a water-gas generator to which air from the blower *b* and steam from the boiler *c* is alternately supplied. *d* is a scrub-

³ Ges. für Linde's Eismaschinen A.-G., First Addition, to French Pat. 427,983, Mar. 31, 1911. See also U. S. Pats. to Carl von Linde 1,020,102 and 1,020,103, Mar. 12, 1912; 1,027,862 and 1,027,863, May 28, 1912; 727,650 and 728,173, May 12, 1903.

⁴ Brit. Pat. 26,928, Nov. 27, 1906.

⁵ Frank (*J. Gasbeleucht.*, June 10, 1911) has recommended (see *J.S.C.I.*, 1911, 746) that apparatus for the production of pure hydrogen and other gases by cooling and liquefaction should be installed at gas works making water-gas to enable hydrogen to be supplied on the large scale.

⁶ Ges. für Linde's Eismaschinen A.-G.

ber and a gasometer. 1 is a water-gas compressor, 2 an air compressor and 3 a refrigerating apparatus. Fore-coolers for drying the air and water-gas are shown at 4. A water-gas separator indicated by 5 is also used for the liquefaction of air. A gas engine 6 operated by the rejected carbon monoxide (collected in gasometer 7) furnishes power for running the compressors. 8 represents purifiers for removal of carbon dioxide and 9 soda-lime purifiers for the ultimate purification of the hydrogen.⁷ Before purification by soda-lime the gas consists of

	Per Cent
Hydrogen	97-97.5
Carbon monoxide	1.7-2
Nitrogen	1.0-1.8

and after such treatment the composition is:

	Per Cent
Hydrogen	99.2-99.4
Nitrogen	0.6-0.8

5811. The Claude Processes. A process for the separation of hydrogen from carbon dioxide has been proposed by Claude.⁸ The hydrogen containing carbon dioxide is subjected to a pressure of, say, 30 atmospheres, and is then passed through heat-exchangers through which cold gas is passing in an opposite direction. The temperature of the gaseous mixture falls progressively, and the carbon dioxide gradually liquefies. The temperature should not be low enough for the production of solid carbon dioxide. The counter-current of cold gas may be the non-liquefied portion of the compressed gaseous mixture, the cold end of the heat-exchanger being cooled externally by suitable means. Claude⁹ partially liquefies water-gas or analogous gaseous mixture so as to give pure hydrogen and carbon monoxide containing hydrogen in solution, and the latter mixture is submitted to the action of heated slaked lime or other material capable of reacting to yield more or less pure hydrogen which is added to the water-gas about to be treated.¹⁰

5812. Claude¹¹ states that in the manufacture of hydrogen by partial liquefaction,¹² hydrogen of 99 per cent purity can be obtained from purified water-gas, but the process is open to objection that the maximum volume of hydrogen obtainable is equal only to one-half the volume of water-gas employed.

⁷ The Bedford method of removing carbon dioxide by washing the gas under high pressure, with water, is used.

⁸ French Pat. 375,991, May 28, 1906.

⁹ French Pat. 453,187, Mar. 28, 1912.

¹⁰ The Claude Company (*Chem. Ztg. Rep.* (1913), 521; French Pat. 453,187, Mar. 28, 1912) indicate that the present attainable yield (about 50 per cent) of hydrogen by the liquefaction system is increased and the loss through solution of hydrogen in carbon monoxide is diminished, if the carbon monoxide gas carrying hydrogen is subjected to the action of hydrated lime to form calcium carbonate and hydrogen, and the impure hydrogen thus secured is mixed with water-gas and further treated in a similar manner.

¹¹ U. S. Pat. 1,135,355, Apr. 13, 1915; French Pat. 453,187; see also U. S. Pat. 1,212,455, Jan. 16, 1917.

¹² French Pat. 329,839.

5813. In practice this yield is reduced owing to part of the hydrogen being held in solution in the carbon monoxide. Also an excessively minute adjustment at the exit cock for the liquefied carbon monoxide escaping from the liquefying apparatus is required, but in practice this cock is generally opened wider than is proper. Claude recommends that the carbon monoxide separated from the water-gas by partial liquefaction be subjected to chemical treatment to produce an approximately equal volume of hydrogen, this hydrogen to be added to further quantities of water-gas to be treated. He makes use of the reaction between carbon monoxide and heated calcium hydrate, affording a volume of hydrogen gas resulting from this step, which is approximately equal to the volume of carbon monoxide gas used. Fig. 168 shows a liquefaction plant of this type.

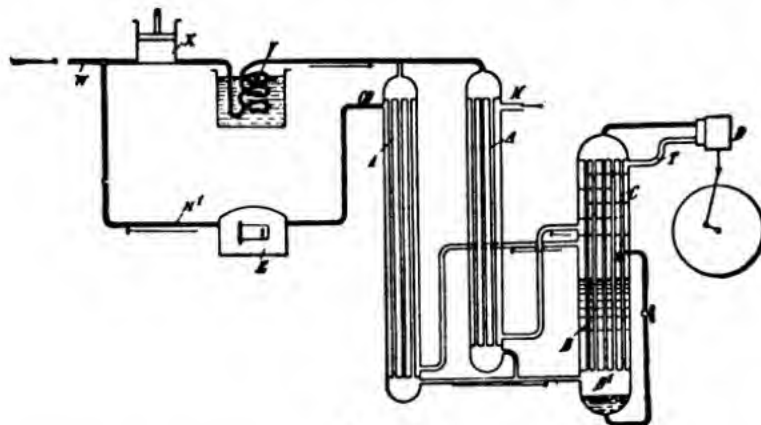


FIG. 168.

5814. In carrying out the process of partial liquefaction, it is necessary to compress not merely the water-gas but the mixture of water-gas and the hydrogen obtained as an equivalent of the carbon monoxide; the ratio of the volumes of the gases in the two cases being about one to one and a half. The nitrogen that the water-gas always contains in greater or smaller proportions accumulates slowly. As soon as this nitrogen attains too great a proportion, it should be removed.

5815. The water-gas to be treated passes through a pipe *W* to the compressor *X* and thence to a cooling coil *Y*, when it passes to two temperature exchangers *AA*. From these exchangers the compressed and cooled water-gas passes upward through the tubes of a carbon monoxide separator *BC*. The lower ends of the tubes are surrounded by the liquid carbon monoxide collected in a chamber *B'* under pressure and discharged into the part *B* under atmospheric or less pressure; the upper ends of the tubes are surrounded by the hydrogen resulting from the separation and expanded in an expansion engine *D*. The hydrogen circulated in the part *C* of the separator passes through one of the exchangers *A* and thence escapes by a pipe *H*, and the vaporized carbon monoxide from the part *B* of the separator passes through the other exchanger and escapes by a pipe *CO*. This carbon monoxide then passes into a chamber *E* where the reaction between the carbon monoxide and calcium hydrate takes place, and the resultant hydrogen passes to the pipe *W* to mix with the incoming water-gas.¹³

5816. In a description of a process of *L'Air Liquide*¹⁴ it is suggested that in order to obtain pure hydrogen by the partial liquefaction of water-gas, the greater part of the carbon monoxide be liquefied by the cold produced by the expansion of the liquefied carbon monoxide from a previous charge. The last traces of carbon monoxide remaining with the hydrogen are liquefied either by the cold produced by the expansion of the whole or a portion of the separated compressed hydrogen, or by the evaporation of liquefied carbon monoxide containing dissolved hydrogen.¹⁵

¹³ See also French Pat. 469,854, May 29, 1913; Brit. Pat. 13,160, 1913; Norwegian Pat. 28,254, Oct. 8, 1917; *Chem. Abs.*, 1918, 520.

¹⁴ Soc. Anon. pour l'Etude et l'Exploit. des Proc. G. Claude.

¹⁵ French Pats. 457,297, Feb. 4, 1914, and 475,346, Feb. 10, 1914; *J.S.C.I.*, 1916, 31. See footnote to para. 5806.

5816A. Claude and Gosselin^{15a} describe a process for producing simultaneously formates and gaseous mixtures rich in hydrogen. The carbon monoxide is a mixture such as is obtained in the partial liquefaction of water-gas and is converted into sodium formate by absorption in a caustic soda solution under a pressure of about 400 atmospheres and at 400°. The residual gases contain a high concentration of hydrogen.

5817. Claude has designed apparatus for effecting the heat exchanges involved in his process for separating hydrogen from such mixtures as coal gas, coke-oven gas and the like.¹⁶ One method is the following: the gas, freed from moisture, carbon dioxide, sulphur compounds and benzol, is passed into the top of a vertical multitubular heat interchanger wherein it is cooled by the passage of previously separated hydrogen upwards through the tubes near the outer casing of the interchanger, and of nitrogen, carbon monoxide, and methane through the central tubes. The more easily liquefiable impurities, such as propane, are liquefied in the upper part of the interchanger and are prevented from solidifying by admixture with liquids which solidify less easily, such as methane, as they flow downwards. The mixed liquids are withdrawn near the bottom of the interchanger and reheated by passage through a coil surrounding the interchanger. If water has not been completely removed from the gas, a small quantity of alcohol vapor may be added to it, and then the alcohol and water are collected in the upper part of the interchanger and removed separately. If the proportion of methane being liquefied is detrimental to the heat balance of the separating apparatus, the mixed liquids are withdrawn at a point further removed from the bottom of the interchanger and passed into the reheating coil. In this case any condensate formed in the lower part of the interchanger may be passed forward with the gas.

5818. Ethylene may be used as a solvent to remove acetylene and some other impurities in the Claude process.¹⁷

5819. Apparently with a view to enriching the gas in nitrogen to fit it for the ammonia synthesis, one of the processes of the Claude Company for treatment of coke-oven gas, etc., is modified as follows.¹⁸ The liquid which contains nitrogen produced in the process is subjected in an auxiliary column to a progressive rectification or vaporization under the pressure of the liquefaction, the gas rich in nitrogen thus produced being returned to the place where the liquid is produced, and the residual liquid substantially free from nitrogen being evaporated to effect the partial liquefaction.

5820. Washing with Liquid Nitrogen. A step apparently due to the Claude Company, but which has been adopted in connection with methods of working

^{15a} U. S. Pat. 1,735,107, Nov. 12, 1929, to La Société chimique de la Grande Paroisse, Azote, et Produits chimiques.

¹⁶ U. S. Pat. 1,579,348, Apr. 6, 1926; Brit. Pat. 195,598, Feb. 26, 1923; Brit. Pat. 195,950, Mar. 15, 1923; Brit. Pat. 238,174, Oct. 21, 1924. See also U. S. Pat. 1,730,805, Oct. 8, 1929, to Claude; *Chem. Abst.*, **1929**, 5519.

¹⁷ Brit. Pat. 230,413, Mar. 8, 1924, to L'Air Liquide, S. A.

¹⁸ Brit. Pat. 235,129, Nov. 4, 1924, to L'Air Liquide, S. A.

other than Claude's¹⁹ is the liquid nitrogen wash.²⁰ The final washing of the compressed hydrogen, to remove carbon monoxide, before expansion, is effected by liquefied nitrogen intended for the lubrication of the hydrogen-expansion engine. The nitrogen is cooled first in heat exchangers, then in tubes by the gaseous carbon monoxide issuing from the vaporizer, and subsequently in tubes situated in the engine exhaust. The liquid nitrogen thus cooled to near its solidification point is passed into a rectifying column wherein it washes the hydrogen. Sufficient nitrogen may be used to allow excess liquid nitrogen to remain with the condensed carbon monoxide, while the vaporized nitrogen mixes with the hydrogen and liquefies in and lubricates the expansion engine.²¹

5821. Liquid air may be used instead of nitrogen, the oxygen being removed by reaction with the hydrogen in presence of a catalyst before the ammonia synthesis.²²

5822. The Linde Company describes a similar step:²³ The residual gas is washed with liquid nitrogen under pressure, whereby the constituents not required are replaced by nitrogen. The washing is effected at nearly constant temperature; the washed gas is then heated by heat exchange with the unwashed gases, and is expanded, the resultant cooling effect being utilized for liquefying nitrogen; or this refrigerating effect may be transferred indirectly to the nitrogen by means of the gas mixture remaining after liquefaction.²⁴

5822A. Hydrogen obtained by the catalytic or thermal decomposition of methane is scrubbed, after removal of carbon dioxide, with liquid nitrogen, preferably under pressure, and is then passed over heated iron, nickel, cobalt, or copper to remove oxygen compounds and dried. The temperature of the liquid nitrogen may be so regulated that 1 volume vaporizes per 3 volumes of hydrogen, thereby yielding a mixture suitable for the synthesis of ammonia.^{24a}

¹⁹ E.g., in the Linde plant described in paras. 5806 and 5828. See para. 5837.

²⁰ Brit. Pat. 234,041, Nov. 31, 1924; Can. Pat. 271,785, June 21, 1927; Brit. Pat. 238,175, Nov. 5, 1924, all to L'Air Liquide, S. A.

²¹ Cf., Lefort des Ylouses, *Science ind.*, 1927, **11**, 53; *Chem. Abst.*, 1929, **23**, 2536; *Brit. Chem. Abst.*, 1928, 891B.

²² Brit. Pat. 250,520, May 26, 1925.

²³ Brit. Pat. 248,377, Feb. 24, 1926. A form of Linde's apparatus is discussed by Bronn [*Z. angew. Chem.*, 1929, **42**, 760-768; *Brit. Chem. Abst.*, 1929, 766B]. In this apparatus, the gas, freed from carbon dioxide by washing successively with water under 12 atmospheres pressure and with caustic soda, is subjected to a preliminary cooling to -30° to -50° by heat interchange with the gases issuing from the apparatus. After entering the actual gas separation apparatus it undergoes further cooling by the already separated gases, whereby all the constituents are condensed except the hydrogen, nitrogen, and part of the carbon monoxide. The residual gas, still under a pressure of about 10 atmospheres, then passes through tubes immersed in a bath of liquid nitrogen boiling under reduced pressure. This brings about condensation of the carbon monoxide and almost all the nitrogen, leaving hydrogen of 98-99 per cent purity. If the gases are required for the synthesis of ammonia the process is slightly modified, the residual mixture of hydrogen, nitrogen, and carbon monoxide being washed with a current of liquid nitrogen under conditions which completely remove the carbon monoxide and leave a mixture of hydrogen and nitrogen in the requisite 3 : 1 ratio. Various possibilities for the economical utilization of the hydrocarbons, e.g., as motor fuels, in the synthesis of alcohols, oils, etc., are discussed.

²⁴ *Brit. Chem. Abst.*, 1927, 629B. Cf. Ger. Pat. 488,416, Feb. 26, 1925, to Ges. für Linde's Eismaschinen A.-G.; *Chem. Abst.*, 1930, 2557.

^{24a} Gasverarbeitungsges. m.b.H., Brit. Pat. 294,580, July 25, 1928; *Brit. Chem. Abst.*, 1930, 325B.

5823. Consideration of the pressure-temperature diagram of different hydrogen-carbon monoxide mixtures leads Cicali²⁵ to the conclusion, which is confirmed experimentally, that, no matter what the liquefaction procedure adopted or the path traversed, the percentage of carbon monoxide present in the issuing hydrogen is invariably connected with the final state of the mixture. Cicali also concludes that direct addition of carbon monoxide to water-gas or a similar gas would injure rather than improve the economic effect (the loss in hydrogen and the work of compression being increased) and the final effect of the purification. Also washing of the ascending gaseous phase by the liquid gradually condensing can never yield hydrogen devoid of carbon monoxide, even if, as Claude suggested, a suitable addition of nitrogen, instead of carbon monoxide, is made to the water-gas or similar gas prior to partial liquefaction of the mixture. On the basis of physical considerations relating to the properties of certain mixtures which are described as physically similar and from which a new principle known as physical substitution is deduced, Cicali suggests the introduction of a definite quantity of gaseous nitrogen, not into the water-gas, but into a mixture derived therefrom, so as to give a mixture similar to, that is, having the same behavior toward liquefaction as, water-gas. The few experimental results as yet available appear to confirm the theoretical results.

5824. Cicali's practical application of his principles is as follows.²⁶ Water-gas is freed from carbon dioxide and hydrogen sulphide, and then further purified to remove the bulk of the carbon monoxide. A volume of free nitrogen equal to the volume of carbon monoxide removed is added to the purified gas, and the mixture is compressed, cooled, and passed into a liquefying machine provided with a fractionating column. The most readily liquefiable component, viz., the carbon monoxide, liquefies in the greatest proportion. The hydrogen and nitrogen contain smaller and smaller quantities of carbon monoxide in the upper parts of the rectifying column. Superimposed upon the rectifying column are tubes surrounded by a mixture of liquid carbon monoxide and nitrogen, super-cooled by evaporation at approximately atmospheric pressure. The hydrogen and nitrogen containing traces of carbon monoxide pass through these tubes, in which the bulk of the nitrogen and the last traces of carbon monoxide condense. The hydrogen, free from carbon monoxide but containing some nitrogen, leaves the refrigerating machine by a coiled pipe surrounding the tube by which the gas to be purified enters.²⁷

5825. In another process²⁸ hydrogen is separated from coke-oven or other industrial gas, after the preliminary removal of water vapor, carbon dioxide, and heavy hydrocarbons, by condensing the remaining components from the compressed gas, utilizing, once the apparatus is in operation, the cold produced by the expansion of the residual hydrogen, and using liquid nitrogen as an additional

²⁵ *Giorn. Chim. Ind. Appl.*, 1926, 8, 171.

²⁶ *Brit. Pat.* 259,643, June 15, 1925, to Cicali; *Brit. Chem. Abst.*, 1927, 43B.

²⁷ *Cf.*, *Brit. Pat.* 291,409, June 1, 1927, to S. A. Brev. Cicali; *Chem. Abst.*, 1929, 23, 1225. The same end is attained by a nitrogen wash; *Can. Pat.* 274,130, Sept. 27, 1927; *Chem. Abst.*, 1924, 18, 4035.

²⁸ *Brit. Pat.* 242,583, Dec. 23, 1924, to Ammonia. *Brit. Chem. Abst.*, 1926, 440B.

external source of cold. The gas mixture is cooled successively in two separators, in one of which the cooling agent is liquid methane, and in the other mainly liquid nitrogen and finally expanded hydrogen. The hydrogen so separated is passed through liquid nitrogen, the expansion of the hydrogen being so adjusted that the two gases issue from the apparatus in the correct proportion for the synthesis of ammonia.

5826. The following is the description of an apparatus and process put forward by the Maschinenbau-Anstalt Humboldt. Water-gas is compressed until the carbon monoxide is liquefied, impurities such as carbon dioxide are removed in the usual manner, and the mixture of hydrogen and carbon monoxide is introduced into a separator *a*, from which it passes through a concentric tube system *b*, in counter-current to the separated cold gases, to a worm *c*, situated in an evaporator *d*, which is partly filled with liquid carbon monoxide. The mixture expands by way of the valved injector *e*, into a condenser *h*, at the bottom of which the liquid carbon monoxide accumulates, while gaseous hydrogen ascends into a riser *i*. Here the entrained carbon monoxide vapor settles by virtue of its greater density, allowing pure hydrogen to pass by way of an overflow-pipe *k* into the concentric tube system *b* and out of the separator at *l*. The liquid carbon monoxide, which accumulates in *h*, passes through an overflow-pipe *m*, controlled by a regulator *o*, down along the chamber *n*, into the evaporator *d*, leaving in the upper part of *n* any accompanying hydrogen, which may be withdrawn. The liquid carbon monoxide, which accumulates at the bottom of *d*, is evaporated by the worm *c*, and the gaseous carbon monoxide escapes by way of the pipe *p*, through the tubular system *b*, and out of the apparatus at *l*. By making the riser *i*, and chamber *n*, of the requisite height, the two gases may be obtained of the required degree of purity.²⁹

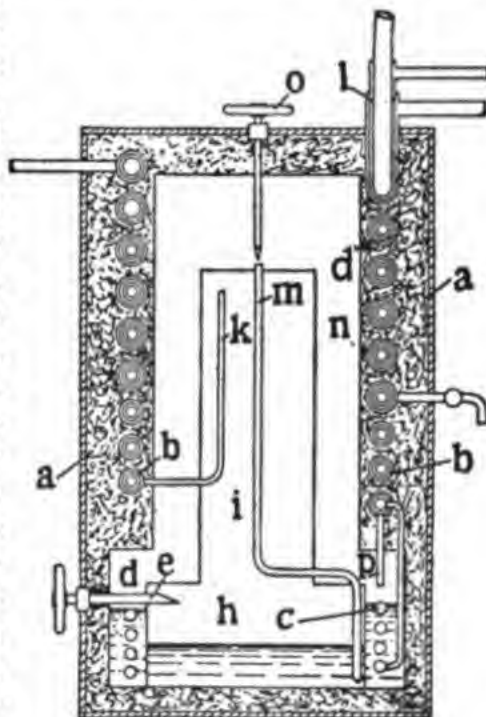


FIG. 169.

5827. While there has been of recent years no revolutionary innovation in the technique of liquefaction for the separation of hydrogen from mixed gases, the application of this method on a colossal scale to the obtaining of hydrogen from coke-oven gas is a novelty of the greatest importance. The subject is most adequately dealt with in a paper describing the process, as applied at Ostend, read by Pallemmaerts before the Second International Conference on Bituminous Coal.³⁰

²⁹ French Pat. 445,883, July 8, 1912.

³⁰ *Chem. Met. Eng.*, 1928, 35, 741.

5828. The cost of hydrogen in the form of coke-oven gas (i.e., the crude material before purification) is lower than that of hydrogen in any other manufactured raw material.³¹ For Belgian conditions the following comparison is made by Pallemerts (*loc. cit.*). One cubic meter of hydrogen: (1) in water-gas, from coke at 170 Belg. fr. a ton, costs 0.62;^{31a} (2) in water-gas from coal at 188 Belg. fr. a ton, costs 0.59;^{31a} (3) in coke-oven gas with the latter at 0.14 Belg. fr., the residual gas being valued at the same price per calorie as the original gas, costs 0.27.^{31a} Therefore, given a supply of coke-oven gas, an economical method of extracting the contained hydrogen and a use or a market for the residual gas,³² this source of hydrogen must be almost without rival for cheapness. The total cost of the *purified* hydrogen at Ostend is 0.665 ^{31a} per cubic meter.

5829. The effect of this on the cost of ammonia synthesis is shown by figures given by Pallemerts. At the Ostend plant ammonia is produced at a cost of 8.7 cents per kilogram of nitrogen in the form of ammonium sulphate (including the cost of sulphuric acid, operation and depreciation). American figures for water-gas synthetic ammonia gave 16 cents per kilogram as the cost of the nitrogen in the ammonia, before transformation into sulphate.

5830. Composition of Coke-oven Gas. According to Walter ³³ coke-oven gas contains approximately:

Hydrogen	46 per cent
Nitrogen	15 per cent
Carbon monoxide	7 per cent
Methane	20 per cent
Ethylene	2 per cent
Carbon dioxide	4 per cent

³¹ Evidently it is not lower than that of the hydrogen contained in hydrogen-rich natural gas.

^{31a} In U. S. cents.

³² The residual gas has a higher calorific value, volume for volume, than the original coke-oven gas. Coke-oven gas contains much hydrogen, which can be readily extracted by a partial liquefaction process such as is being worked at Ostend and elsewhere, according to Furness [*Chem. Age* (London), 1929, 279]. At Ostend, coke-oven gas is taken and paid for at current rates and is subjected to purification and partial liquefaction. Benzene, ethylene, and propylene are recovered, and essentially all but the hydrogen is at length liquefied. By scrubbing the residual gas with liquid nitrogen, Furness states that pure hydrogen is finally obtained at a cost of around ten pence per 1000 cubic feet. The methane, etc., which remains after the extraction of the hydrogen represents about 70 per cent of the original calorific value of the coke-oven gas and is delivered to the city mains, credit being given for the calorific value of the gas returned. This is stated to be higher than the original in calorific value. Furness proposes that coke-oven gas be collected from the various ovens throughout a given area, deprived of its benzene, ethylene, etc., and fractionated into pure hydrogen—producible at a low cost—and methane. Processes are available for further utilization of the methane residuals. Thus, by thermal decomposition in a water-gas producer (the methane being passed in place of the steam ordinarily used for actual water-gas production over incandescent coke) hydrogen requiring little purification has been made.

³³ *Seifen. Ztg.*, 1913, 4. The presence of nitrogen peroxide in coke-oven gas has been established and its concentration determined colorimetrically by using a solution of *m*-phenylenediamine. Nitric oxide, however, formed the greater proportion of the oxides of nitrogen present in the gas. This was determined by the addition of oxygen, whereby it is partly converted into nitrogen peroxide. The concentrations found were of the order of 0.0001–0.003 per cent. The results were confirmed by hydrogenation of the nitric oxide over copper and determination of the ammonia formed. The presence of the nitric oxide was traced to the flue gases, which may contain up to 0.2–0.4 per cent, and are drawn into the chambers by the suction of the exhaustor. Schuftan, *Z. angew. Chem.*, 1929, 42, 757–60; *Brit. Chem. Abst.*, 1929, 765B.

5831. Choice of Methods. The choice of processes for separating the hydrogen lay between the steam-iron process and one of the liquefaction processes. Pallemmaerts does not say why the catalytic process was not considered, but one may surmise that the high content of hydrocarbon would be unfavorable to satisfactory operation. The smallness of the steam-iron units and the impurity of the gas yielded are given as the reasons for rejecting this process, though here, again, the hydrocarbons would be a cause of trouble. Between the Claude system of fractionation and the Linde system the choice fell on the latter. Among the determining factors was the greater purity of the Linde product.

5832. Purification. Preliminary work brought out the necessity for dryness of the gas and freedom from carbon dioxide. Water and the dioxide, solidifying in the tubes, caused obstructions. Desulphurization was also necessary. After trying out the usual purifying train: iron oxide boxes; water washing under compression; washing with caustic soda; drying under pressure over calcium chloride, a short cut was taken. An ammonia washing process, operating at atmospheric pressure, was used to remove both carbon dioxide and sulphur compounds, drying being left to be effected by the first refrigeration. This, after some trial and error, was successful, better purification being attained than with the usual complex train. This was not the end of the troubles, however, as obstructions and local explosions occurred. These were traced to the presence of unsaturated hydrocarbons which solidified in the pipes. This source of trouble was eliminated by a pressure water wash. Although the plant now ran smoothly it was found desirable to remove oxides of nitrogen and volatile nitro-compounds. This was effected by a "simple physical treatment of the gas" of which no further description is given by Pallemmaerts.³⁴

5833. The residual gas contains methane, ethylene and their homologs. It is free from sulphur compounds and is anhydrous. The removal of the hydrogen has produced an increased calorific value, for a given volume, of 43.5 per cent. As a fuel gas it is of notable value. Owing to its purity it may be utilized in organic syntheses. For the present, however, it is used to heat the coke-ovens and, where a large quantity of hydrogen must be got from a small quantity of coke-oven gas, it can be made a source of hydrogen by employing one of the processes described in the section on the manufacture of hydrogen by decomposition of hydrocarbons.

5834. This last mentioned step is specifically described by Battig.³⁵ The hydrogen present in coke-oven gases is separated from the other constituents by liquefying the latter. The liquefied gases are then fractionated, and a further supply of hydrogen is obtained by the thermal decomposition of the methane fraction. The decomposition is carried out by passing the methane over highly heated coke in a generator or in the chambers of a coke-oven. If the decomposition is incomplete the resulting gases may be again subjected to separation by liquefaction.

5835. The French company which operates the Claude processes has

³⁴ See para. 5835.

³⁵ Brit. Pat. 271,491, May 19, 1927; *Brit. Chem. Abst.*, 1928, 470B.

described a step in the purification of coke-oven gas by hydrogenation, whose object is the removal of oxides of nitrogen. The catalysts used are copper or iron ("which has been used in the synthesis of ammonia"), the temperature required is low and the operation takes place at atmospheric pressure. Acetylene is hydrogenated, ethylene unaffected. Hydrogen may be obtained by liquefaction.³⁶

5835A. In separating hydrogen from coke-oven gases by liquefaction the nitrogen-oxygen compounds in the mixture may be preliminarily removed. This may be done with ammonium sulphate solutions, or by catalytic hydrogenation.^{36a}

5836. In a process due to van Nuys³⁷ a mass of ignited carbon is subjected to the action of steam and oxygen in a gas producer, and the resulting gas is separated into its constituents by liquefaction, the oxygen for the producer and the refrigerating agent for the liquefaction process being thereby produced at the same time.

5837. Coke-oven gas is compressed to 10 atmospheres and the carbon dioxide, hydrogen sulphide, etc., are removed; the purified gas is then cooled in a counter-current heat exchanger so that the higher-boiling constituents separate.³⁸ Most of the methane is subsequently condensed in other coils around which circulates additional compressed nitrogen; the cooling effect produced by evaporation of the methane is thus transferred to the nitrogen and carried to another point, when the latter evaporates at a lower pressure. After this treatment the residual gas is rich in carbon monoxide and hydrogen; the former is readily condensed, and the hydrogen is finally purified by washing with liquid nitrogen.

5838. Hydrocarbon gas mixtures containing at least 60 per cent hydrocarbons are freed from hydrogen and catalyst poisons by cooling to a low temperature and fractionating. Water vapor is added, and the mixture passed over a highly sensitive catalyst at about 500° C. A mixture of hydrogen and carbon dioxide is obtained and is purified in a similar manner. The unconverted hydrocarbons are returned to the process.³⁹

5839. If the removal of carbon monoxide were necessary in order to make coal-gas non-poisonous, three methods are available: (1) absorption, (2) catalytic process, or (3) condensation. Kemmer⁴⁰ concludes that absorption with ammoniacal copper formate solution, catalytic conversion into methane, and fractional distillation are all technically possible.

³⁶ Brit. Pat. applications 287,558 and 287,577, convention date, Mar. 25, 1927; *Chem. Age* (London), 1928, 18, 495.

^{36a} Ger. Pat. 484,055, June 2, 1927, to Société L'Air Liquide (Soc. Anon. pour L'Etude et L'Exploitation des Procédés Georges Claude); *Chem. Abst.*, 1930, 902.

³⁷ U. S. Pat. 1,588,860, June 15, 1926, assigned to Air Reduction Co.; *Brit. Chem. Abst.*, 1926, 708B.

³⁸ Ges. f. Linde's Eismaschinen A.-G., Brit. Pat., 284,213, Jan. 21, 1928; *Brit. Chem. Abst.*, 1929, 933B.

³⁹ Ges. f. Linde's Eismaschinen Akt.-Ges., Brit. Pat. 317,731, convention date Aug. 20, 1928; *Chem. Age* (London), 1929, 388. See also *Chem. Abst.*, 1930, 2254.

⁴⁰ *Gas- u. Wasserfach*, 1929, 72, 744; *Brit. Chem. Abst.*, 1929, 765B.

CHAPTER LIX

HYDROGEN (IV.)

HYDROGEN FROM HYDROCARBONS

5900. Hydrocarbons are, next to water, the greatest natural source of hydrogen. Many methods have been practiced for the manufacture of hydrogen by the decomposition of hydrocarbons. These processes may be divided into two classes: the first depends on thermal decomposition of the hydrocarbon; the second, on the reaction with steam. Closely related to the steam reaction processes are methods employing partial combustion as a step (*cf.* para. 5938).

HYDROGEN FROM HYDROCARBONS BY THERMAL DECOMPOSITION

5901. When methane is heated to 1200° to 1300° C. dissociation occurs and lamp-black and hydrogen are produced. Acetylene is decomposed at a much lower temperature. In general, when subjected to sufficient heat hydrocarbons break down into their elements. This fact has been made use of for the production of hydrogen by decomposing various hydrocarbons and particularly heavy oils. Among the proposals put forward up to the present time are some which relate to the splitting of acetylene or natural gas by passage through the heat zone of an electric arc and separation of the hydrogen from the lamp-black or other carbonaceous material which is formed. The gas may be under pressure to render the decomposition more effective.

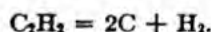
HYDROGEN FROM ACETYLENE

5902. Pictet ¹ decomposes an endothermic hydrocarbon, such as acetylene, by passing it through a tube, the front portion of which is heated to about 500° C., at which temperature the gas dissociates into its elements with the evolution of a large quantity of heat. The latter raises the temperature of the tube sufficiently to dissociate fresh quantities of acetylene without the further application of external heat. The rear portion of the tube is surrounded by a refrigerating appliance, and the products of decomposition, hydrogen and lamp-black, are passed into a apparatus suitable for their separation. The generator may consist of a steel, iron or porcelain tube, one portion of which is heated by means of a gas furnace, and the other cooled by water, or by a liquid hydrocarbon, the vapors of which are afterwards admitted to the tube for their dissociation. The tube is provided with the conduits necessary for the admission of the raw mate-

¹ French Pat. 421,838, Oct. 26, 1910.

rials and for the withdrawal of the products of dissociation, these conduits being preferably composed of "pure iron" covered with nickel; the lamp-black is separated by washing or by means of filters.

5903. A process worked out by the Carbonium Company in Germany employs acetylene gas which is compressed to two atmospheres and exploded by an electric spark.²



The acetylene thereby dissociates into the elements carbon and hydrogen. The carbon deposits in the form of lamp-black. The hydrogen is passed through a large washer and stored. Its degree of purity is exceptionally high. For each cubic meter of hydrogen produced about 1 kilo of lamp-black is formed. A condition for getting the hydrogen cheaply by this method is that there be a market for the lamp-black.

5904. Similarly, Wachtolf³ compresses the acetylene to about 4 to 6 atmospheres and explodes it electrically. In Fig. 170 the explosion chamber is shown on the left and lamp-black collector on the right. The explosion chamber is provided with a rotary scraper to remove lamp-black adhering to the walls.⁴

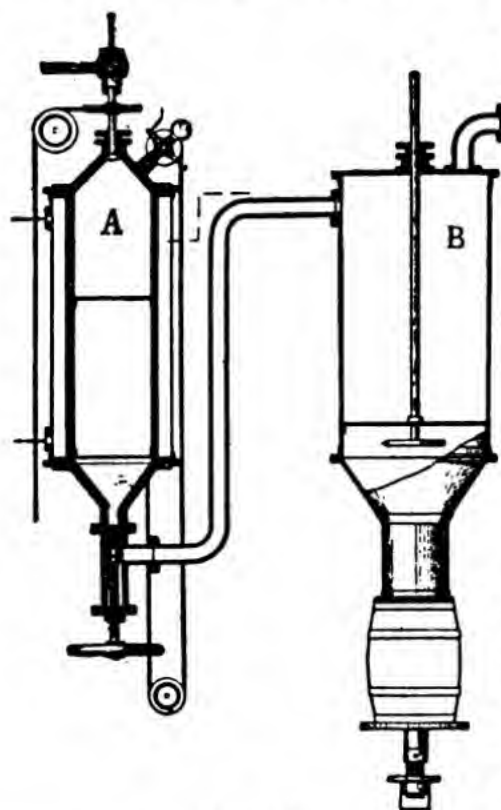


FIG. 170.

OTHER HYDROCARBONS

5905. Geisenberger⁵ generates hydrogen alone or mixed with carbon monoxide or carbon dioxide, by the action of heat alone or of heat and steam, on light hydrocarbons, such as benzene, or on other materials containing hydrogen and carbon, e.g., bitumen, shale, beeswax, turpentine, etc. The organic substance is heated in a retort, to which steam may be admitted, to its point of decomposition. The hydrogen is separated from the other gases in the mixture obtained, either by physical means,

depending on the differences in density, or by chemical means, such as absorbing the carbon dioxide by means of sodium carbonate or hydroxide solution.

5906. Rincker and Wolter⁶ make use of two generators, somewhat resembling those used in making water-gas, for the decomposition of oils and tars. These generators are arranged side by side and charged with coke. After they have been raised to incandescence by a blast of air, a charge of tar is introduced into

² *Met. and Chem. Eng.*, 1911, 157.

³ Ger. Pat. 194,301.

⁴ Decomposition of hydrocarbons under pressure is described by Bosch, Ger. Pat. 268,291 July 14, 1911.

⁵ French Pat. 361,492, Dec. 21, 1905.

⁶ French Pat. 391,868, May 11, 1908.

one of them and is partly transformed into gas by the glowing fuel. The gas formed escapes by its own expansion. A current of air is then introduced which carries forward the remaining vapors of tar into the second generator where they are converted into a permanent gas. At the same time the blast of air raises the contents of the first generator to incandescence again, and the process is reversed by introducing the tar into the second generator and repeating the operations in the reverse direction.

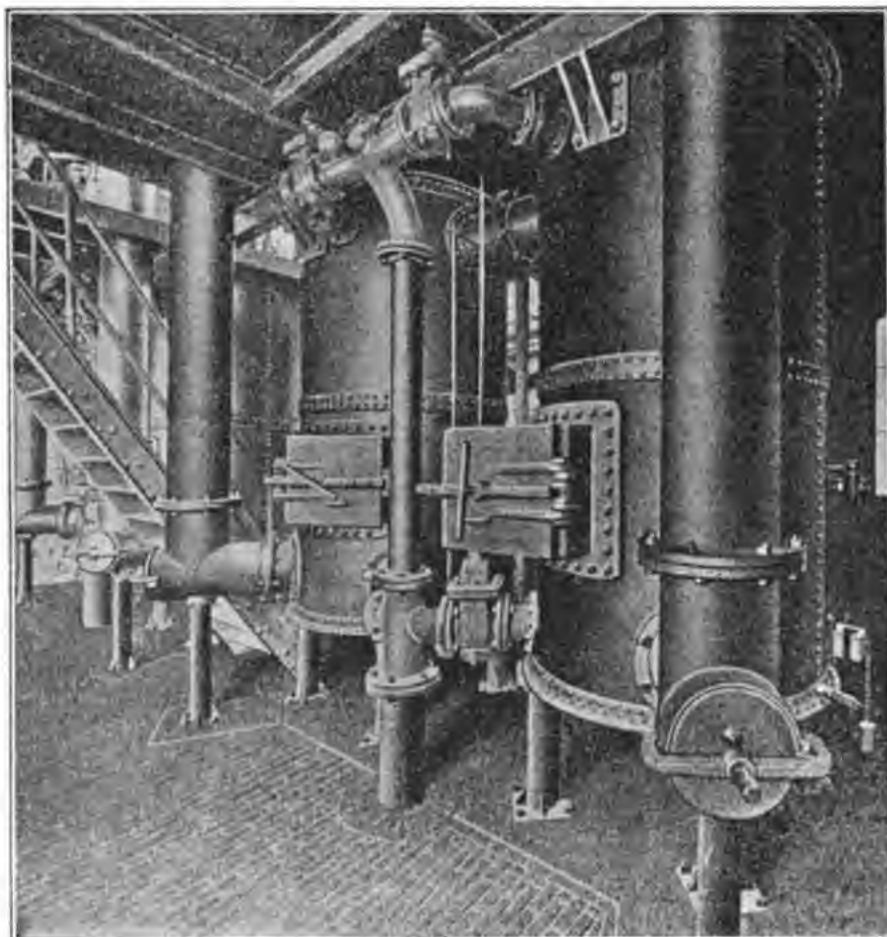


FIG. 171.

5907. In a modified form of the apparatus ⁷ the two generators are arranged one above the other and are charged with coke. The coke in the lower generator is ignited and then brought to incandescence by a blast of air which has been preheated by being caused to pass through a jacket surrounding the upper generator. The fuel in the latter is also ignited and then raised to incandescence by natural draught. The products of combustion are allowed to escape to the chimney. When the fuel is glowing brightly, the air supply is cut off and a charge of

⁷ French. Pat. 391,867, May 11, 1908.

oil is introduced into the lower generator through pipes in the top. The oil passes over the glowing fuel and is partially converted into permanent gas which escapes through a pipe in the side by its own expansion. The blast of air is then again turned on, whereby the vapors of oil left in the lower generator are blown into the upper one, where they are gasified and fixed during their passage through the glowing fuel. The lower generator is at the same time again raised to incandescence and the process is repeated.⁸

5908. Equipment for the Rincker-Wolter system has been supplied by the *Hollandsche Residugas-Maatschappij* of Rotterdam. The gas-making plant consists of twin generators,

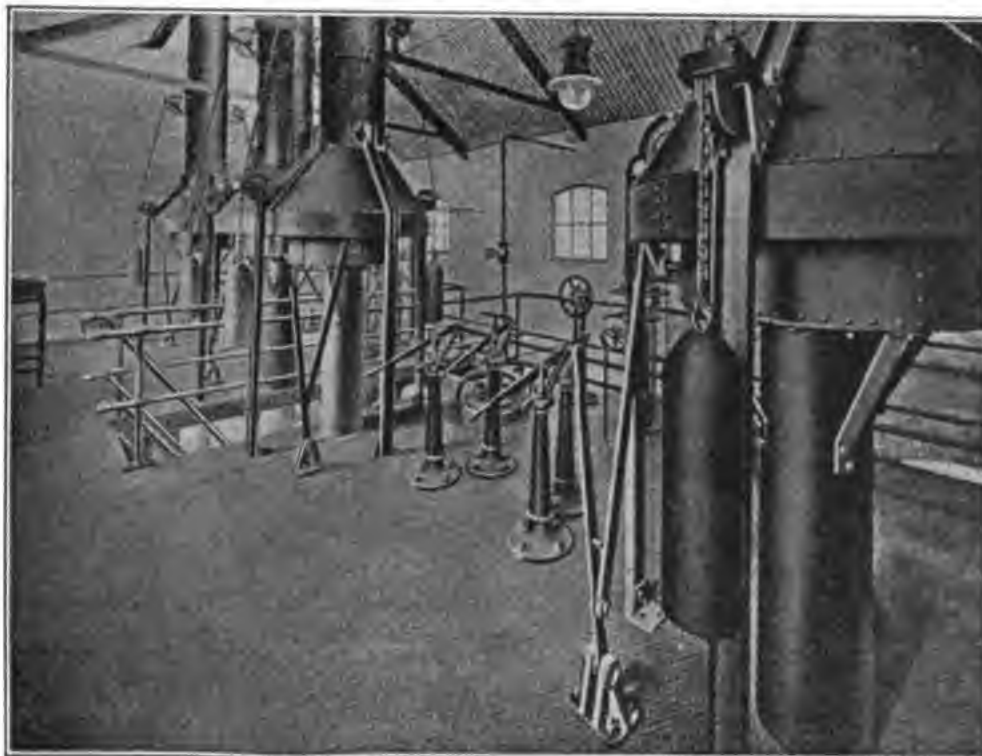


FIG. 172.

Fig. 171, lined with firebrick and provided with grate bars and clinkering doors; in short resembling water-gas generators but lacking a carburetor and superheater. The generators are connected near the top and in the upper part are lids for feeding purposes, which carry sprayers for introduction of the oil. Fig. 172 shows the operating floor of one of these plants. The generators are equipped with primary and secondary blast pipes, steam inlets and dust collectors. Both generators are charged with coke and fired. The generators are operated alternately in the blowing-run, the first generator receiving the primary, and the second generator the secondary, air blast. Combustion is incomplete in the first generator and the producer gas obtained is led to the second generator, where it is burned on meeting the current of secondary air, thus heating up the second generator.

⁸ Apparatus for the production of hydrogen by the decomposition of the vapors of oil or tar by exposure to a high temperature is the basis of a patent to the *Berlin-Anhaltische Maschinenbau Aktien-Gesellschaft*, Berlin, Ger. Pat. 267,944, Jan. 28, 1913; *Chem. Zeit. Rep.*, 1914, 31.

5909. As it is preferable to reach nearly equal temperatures in both generators, the sequence is reversed after a short blowing and the first generator becomes second in the series. When both generators have reached the proper temperature, the air valves are shut and the gas run begins. The temperature of the fuel bed has to be varied somewhat according to the nature of the raw materials. For hydrogen production a temperature of about 1200° C. is required. Too low a temperature gives so impure a gas that subsequent purification of the hydrogen is rendered costly. At the end of the blowing-run oil is sprayed for several minutes on the hot coke and gasification takes place. Immediately after this the sprayer is cleaned by blowing steam through it. The gas formed by decomposition of the oil passes to a seal and from there to scrubbers and purifiers.

5910. Fig. 173 shows the gas outlets and seal. The residue of gas in the generators is expelled by steam. Lamp-black is deposited in the generators and is consumed in the next run. Fig. 174 shows the generators of a plant at Utrecht.

In a well-handled run gas of the following composition is said to be obtained:

	Per Cent.
H.....	96.0
N.....	1.3
CO.....	2.7

And by passing this gas over heated soda-lime a gas has been secured analyzing:

	Per Cent
H.....	98.4
N.....	1.2
CO.....	0.4 ⁹

5911. To avoid difficulties from clinkering of the ash of the fuel, the author has suggested the addition of a small proportion of lime to the charge of coke, so as to flux the ash and thus to enable the maintenance of the requisite high temperature in the fuel bed.¹⁰

5912. By a modification of the Rincker-Wolter process¹¹ liquid hydrocarbons are converted into oil-gas, on contact with glowing coal or coke in the customary manner, and water-gas or other gas containing hydrogen is led into the oil-gas generator with the object of converting the oil residues into hydrocarbons that can be gasified. The formation of tar in the oil-gas generator is thus avoided. Two generators are used, each serving as a water-gas generator and an oil-gas generator alternately.¹²

5913. A portable plant of the Rincker-Wolter type, which may be used for military purposes, is arranged so compactly that it may be mounted on two ordinary railway flat cars. The apparatus consists of two gas producers in which hydrogen is made from oil which is sprayed into the producer. The gas is then passed through purifiers and driers to give hydrogen of the desired purity. In case it is necessary to compress the gas a third car is needed.

5914. Bacon, Brooks and Clark¹³ have devised a process for obtaining carbon black, and practically pure hydrogen, by the decomposition of hydrocarbons, the conditions of working being such as to insure a satisfactory yield of both products in a continuous operation. The apparatus employed is adapted to develop and maintain the high temperatures required and withstand, during long-continued use, the exacting requirements imposed upon it.

5915. Bacon, Brooks and Clark state that unless the carbon black produced as one of the products of the decomposition is promptly removed from the high temperatures (exceeding 1200° C.) of the heating zone in which the decomposition is proceeding, such carbon black will deteriorate in quality for commercial uses, losing its desired deep-black luster, and becoming materially duller and grayer. Accordingly, the operation is conducted so that the

⁹ Sanders (*Zeitsch. f. angew. Chem.*, 1912, 2404) has furnished figures on the cost of hydrogen by the Rincker-Wolter system. In a private communication to the author, the manufacturers advise that with oil at 4 cents per gallon the hydrogen is estimated to cost about \$1.75 per thousand cubic feet.

¹⁰ Ellis, U. S. Pat. 1,092,903, Apr. 14, 1914.

¹¹ Brit. Pat. 6,285, Apr. 27, 1915.

¹² *Scientific American Suppl.*, Sept. 5, 1914, 155.

¹³ U. S. Pat. 1,220,391, Mar. 27, 1917. See also No. 1,276,385, issued Aug. 20, 1918, to McCourt and Ellis. See para. 5919.

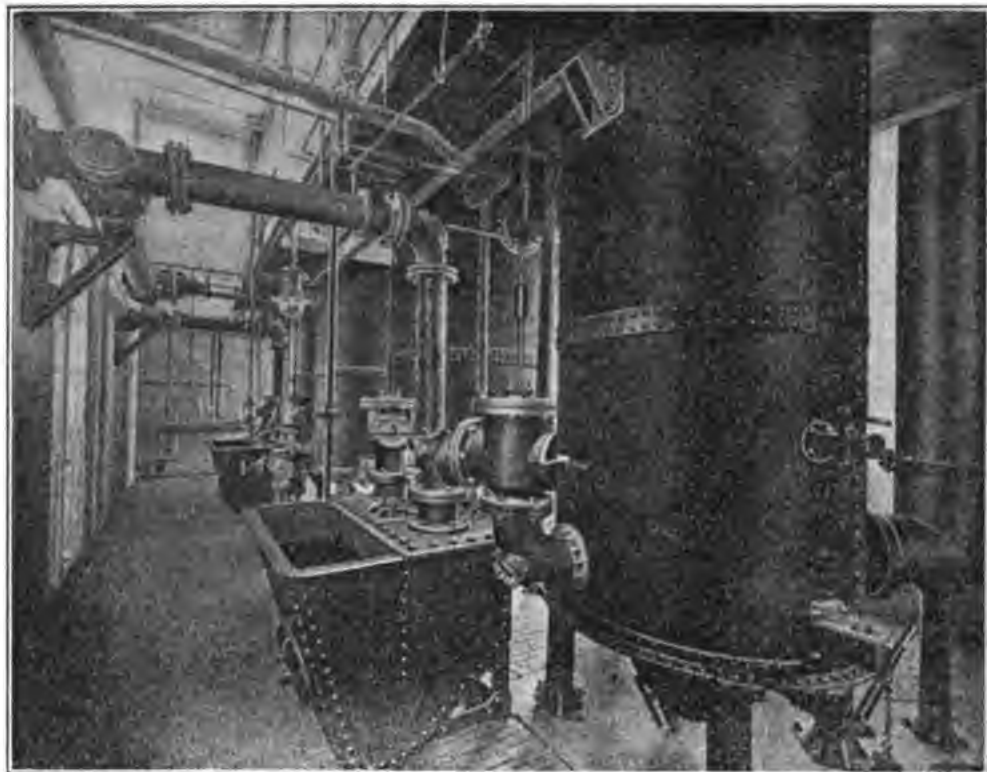


FIG. 173.

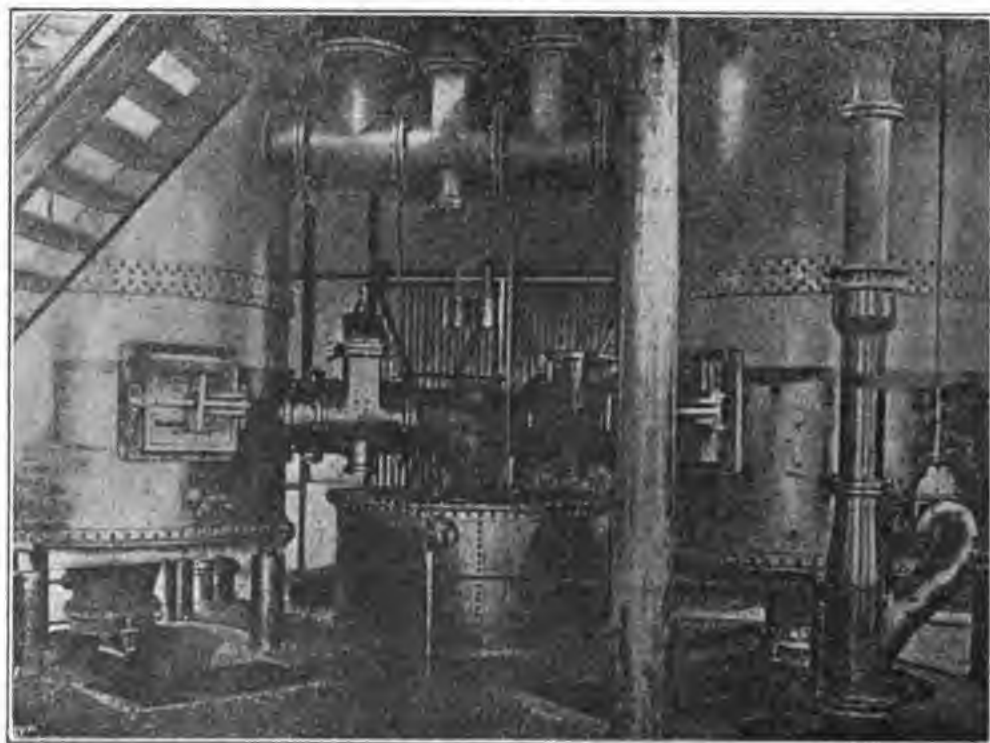


FIG. 174

particles of carbon black will remain suspended in the hydrogen, and are removed with the hydrogen from the zone of decomposition.

5916. In Fig. 175 is shown a gas-tight metal shell, having a gas-tight cover. The casing is provided at one end with an exit pipe for the outflow of the carbon black and hydrogen, and has an opening at its opposite end closed by a removable gas-tight asbestos board closure. Within the casing is a lining of fire-brick and an inner lining of magnesite brick. In the chamber is located the heating element which is made up of a double series of graphite rods cut in two diametrically. Through stuffing boxes of the face plate there extend carbon rods,

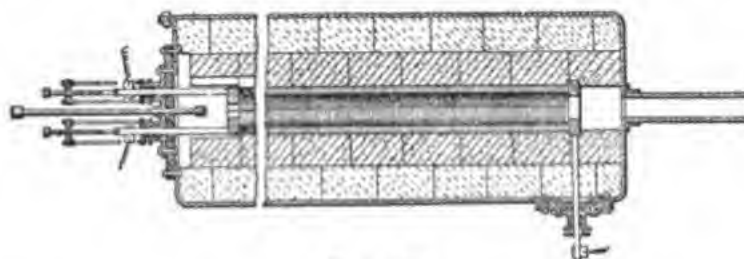


Fig. 175.

each of which is connected to the same terminal of an electric heating circuit. The hydrocarbon to be decomposed is supplied in a thin stream through the inlet pipe on the left. It enters the decomposition zone of the apparatus, made up of the annular walls of the series of graphite rings, which rings are heated by an electric current to a temperature exceeding 1200°C . and sufficient to flash and decompose the hydrocarbon into carbon black and hydrogen. The temperature of flashing or decomposition, and the quantity of liquid hydrocarbon

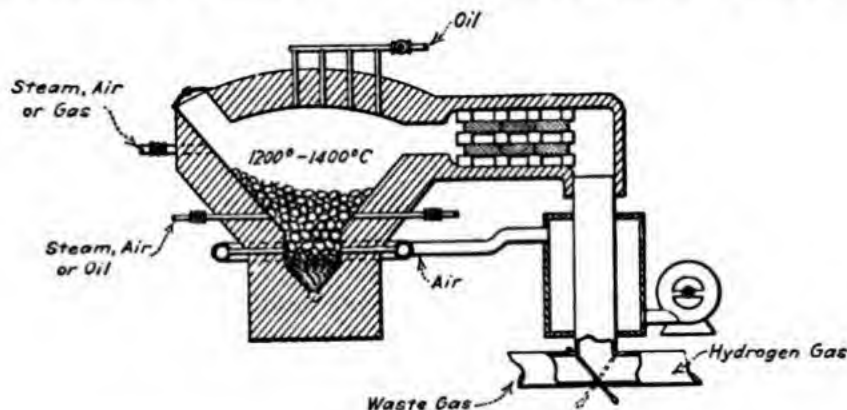


Fig. 176.

injected are so adjusted that the gas pressure developed shall be sufficient to sweep out the particles of carbon black without permitting them to settle in the decomposition zone of the apparatus. The carbon black is deposited in a settling chamber, and the hydrogen is carried on to a gas holder. The carbon black recovered is of a black silky luster, and the hydrogen is substantially pure.

5917. Ellis describes ¹⁴ a type of furnace connected to a checker-work chamber, to be used for the heat decomposition of oils to yield hydrogen. A bed

¹⁴ U. S. Pat. 1,092,903, Apr. 14, 1914. Natural gas, cracked in a water-gas set by using it in place of steam after the blast, will furnish a gas containing 90 per cent hydrogen and less than 10 per cent hydrocarbon. About 2.25 cu. ft. of cracked gas may be produced per cubic foot of natural gas with a stated consumption of 0.015 lb. of coke. Yunker, *Gas Age-Record*, 1929, 63, 674, 680; *Chem. Abst.*, 1929, 4555.

of coke in the furnace is heated to white heat and hydrocarbon oil enters above

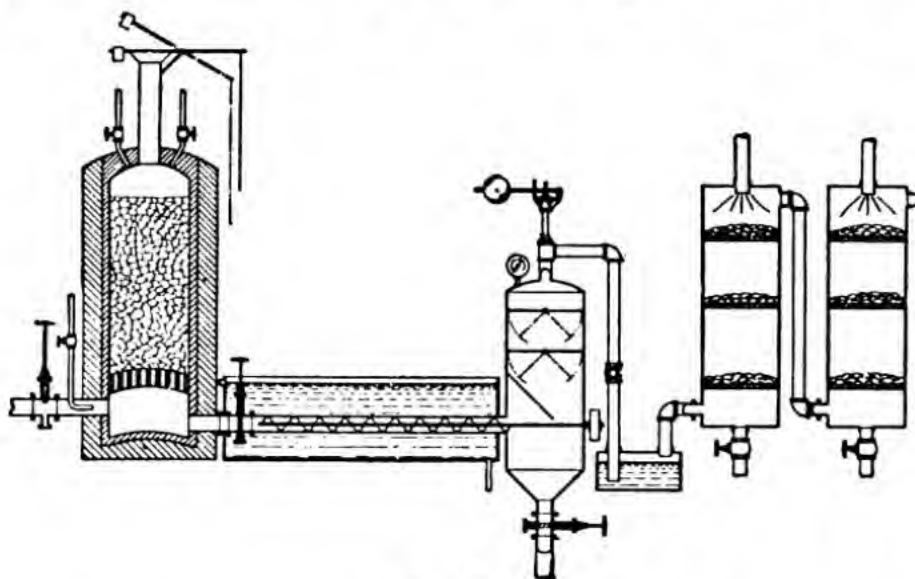


FIG. 177.

the bed where it is decomposed. The vapors pass through the heated checker work and are further decomposed. The furnace is provided with air and steam inlet pipes for blowing up the fire and for sweeping out contaminating gases. Fig. 176 shows this form of apparatus.

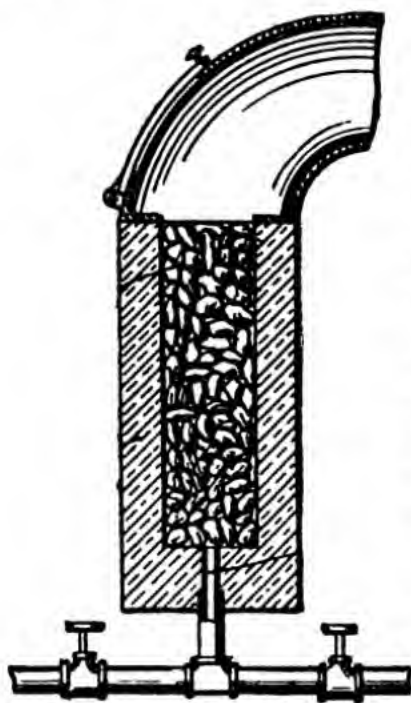


FIG. 178.

5918. Brownlee and Uhlinger¹⁵ describe a process of producing hydrogen and carbon black which consists in passing hydrocarbons, at a pressure above atmospheric, over a highly heated mass of refractory material which is free from easily reducible metallic oxides. The refractory material is first heated to about 1400° C. and then gas or oil vapors passed in from the top. The carbon is collected in a chamber and removed as collected by means of a screw conveyor. The hydrogen is purified if necessary and passed into a gas heater. Any carbon which may be deposited on the refractory material will be burned off on reheating for further decomposition. Fig. 177 shows a diagram of the apparatus.

5919. McCourt and Ellis¹⁶ obtain gas-black and hydrogen by forcing methane

¹⁵ U. S. Pat. 1,168,931, Jan. 18, 1916, 1,265,043, May 7, 1918, and 1,276,487, Aug. 20, 1918.

¹⁶ U. S. Pat. 1,276,385, Aug. 20, 1918; Can. Pat. (to McCourt) 187,661, Nov. 26, 1918.

through a highly heated porous and permeable bed of refractory material. One form of apparatus employed is illustrated in Fig. 178.

5920. Although acetylene is easily decomposed at temperatures such as prevail in the processes which we have been describing, it is relatively stable at the temperature of the electric arc.¹⁷ Advantage is taken of this to produce pure hydrogen from mixtures containing hydrogen and methane.¹⁸ The mixture (e.g., methane 14 per cent, hydrogen 86 per cent) is passed through a furnace arc to produce a gas containing acetylene 7, and hydrogen 93 per cent, which is withdrawn by a special device. The acetylene is removed by washing.

5921. Barth¹⁹ produces hydrogen by first decomposing oil in a furnace and then further heating the gas formed in a separate furnace to produce hydrogen. He claims for this method that there is an economical use of fuel and that the contact mass in which the hydrogen is formed does not become contaminated with carbon, etc.

5922. The furnace or vaporization chamber used by Barth, see Fig. 179, is constructed of an iron jacket which has a lining of refractory bricks, and which is filled with a refractory grating or with coarse pieces of refractory material. The gases of combustion which escape from the generator during the blowing or reheating period are passed through the refractory grating of the vaporization chamber. Near the end of the blowing period the gases contain a certain amount of carbon monoxide which is burnt within the vaporization chamber by admitting air thereto. By this operation the grating of refractory material within the vaporization chamber accumulates the heat which is necessary for vaporizing the liquid fuel and in some cases for partly decomposing the same. Finally the air supply is shut off, and the vaporized oil or other fuel is passed into the vaporization chamber through several nozzles and vaporized therein. The vapors are passed through the glowing charge of coke within the generator, where they are decomposed in such a way as to split off carbon and to produce either an illuminating and heating gas (if the process is carried out at a temperature of about 1000° C.), or hydrogen (if the process is carried out at a higher temperature). The vapors of oil or other fuel are alternately passed through the generator in opposite directions, that is, alternately from above downward and from below upward. Thereby the heat which has been accumulated within the generator is uniformly consumed, and the lower part of the generator which, during the blowing period, is subject to the highest strain is not brought to an excessive temperature.

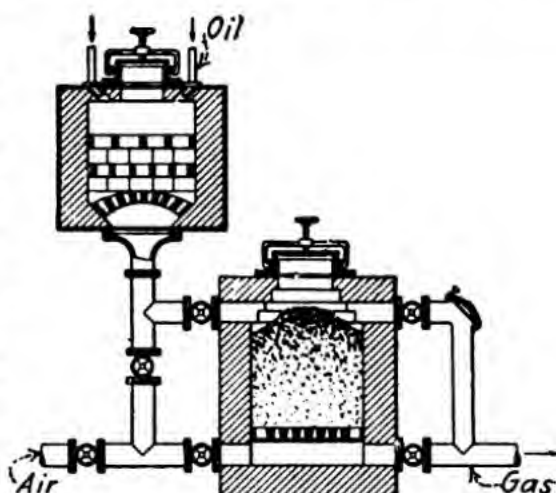


FIG. 179.

¹⁷ For a discussion of the equilibria see: Taylor, *Industrial Hydrogen* (Am. Chem. Soc. Monograph), 1921, 148-149.

¹⁸ Brit. Pat. 288,056, Dec. 30, 1926, to I. G. Farbenind. A.-G. (this is an addition to 263,859 in which the apparatus is described); *Chem. Abst.*, 1929, 23, 488; *Brit. Chem. Abst.*, 1928, 415B. Petroleum or coal-tar oil has been decomposed into hydrogen and acetylene (and small quantities of methane, ethylene, and carbon monoxide) by circulating it around an electrically heated conductor at temperatures above 800°. The gaseous mixture as it is evolved is quickly cooled to prevent the decomposition of the acetylene. Bethenod, Brit. Pat. 316,905, April 4, 1928; *Brit. Chem. Abst.*, 1929, 804B.

¹⁹ U. S. Pat. 1,172,925, Feb. 22, 1916.

5923. A process of producing hydrogen gas or gas containing this constituent is proposed by Lowe³⁰ which involves heating a bed of solid fuel to incandescence and passing into the ignited mass a quantity of petroleum oil which breaks down into hydrogen and carbon. The hydrogen is removed and the deposit of carbon is subjected to combustion with an amount of air sufficient only to consume part of the carbon which has been deposited. Then further quantities of petroleum oil are injected into the fuel mass.³¹

5924. Snelling³² employs carbon compounds which are capable of dissociation by heat in a reversible manner, with the liberation of hydrogen. These compounds are heated in a closed chamber or tube with walls more permeable by hydrogen than by other substances present, and the hydrogen formed is thus withdrawn during the reaction.³³

5925. An apparatus for producing hydrogen from natural gas, crude petroleum or garbage grease designed by Brunner³⁴ employs a series of vertical stand pipes alternately connected at top and bottom and internally sprayed with water to remove carbon and other impurities. The water is finally discharged through a liquid seal at the bottom of each pipe. (See Fig. 180.) The organic material is heated in an adjacent furnace (not shown).

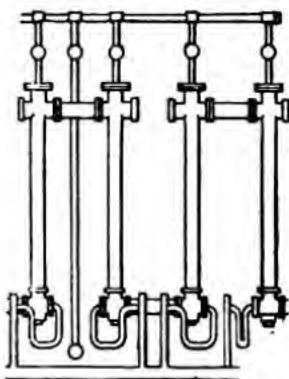


FIG. 180.

5926. Pictet,³⁵ in the production of a gas of high heating value, heats crude petroleum, tar oil or similar hydrocarbons in tubes to such a temperature (e.g., 900° to 1200°), that not all the hydrogen splits off as such, but appears in the end product as methane. The hydrocarbons to be broken down may be employed mixed with gases of less heat value, such as hydrogen, water-gas, etc.

5927. Frank³⁶ passes purified natural gas through a furnace filled with incandescent coke or refractory material thereby producing hydrogen. Natural gas is first freed of hydrogen sulphide by passage through a purifier which contains an iron oxide, such as limonite. Thereupon the gas is subjected to a temperature of at least 1200° C. The decomposition of the gas begins at a temperature of about 800° C., while the gas is completely split into carbon and hydrogen when the highest temperature, exceeding 1200° C., is attained. See Fig. 181.

5928. Rose³⁷ prepares gas containing as high as 98 per cent hydrogen by passing natural gas or oil over refractory surfaces heated to 1650° C.

5929. The production of hydrogen and soot by the pyrogenic breaking down of light hydrocarbons, especially natural gas, by contact with highly-heated refractory surfaces, against which the gas under treatment is directed in a number of finely divided currents, is described by Herman.^{37a} With the exclusion of air, the baking and graphitizing of the soot on the surfaces may be prevented by a uniform heating of the surfaces serving for the decomposition and a careful removal of the soot from the heated surfaces after its formation. The hydrogen is drawn off and cooled immediately.

5930. Efforts to secure hydrogen from illuminating gas have met with a considerable measure of success. By the process of Oechelhauser hydrogen of about

³⁰ U. S. Pat. 1,174,511, Mar. 7, 1916.

³¹ See also Frisch, U. S. Pat. 1,118,899, Nov. 24, 1914.

³² *J.S.C.I.*, 1915, 249; U. S. Pat. No. 1,124,347, Jan. 12, 1915.

³³ See also *O. P. & D. Reporter*, Apr. 5, 1915, 34.

³⁴ U. S. Pat. 1,246,867, Nov. 20, 1917; *Chem. Abs.*, 1918, 297; *J.S.C.I.*, 1918, 30A.

³⁵ Ger. Pat. 277,115, Feb. 13, 1913. Addition to 257,715; *Chem. Abst.*, 1915, 712; Ger. Pat. 289,065, Dec. 7, 1912. See also Can. Pat. 184,460, May 21, 1918.

³⁶ U. S. Pat. 1,107,926, Aug. 18, 1914; *Chem. Abs.*, 1914, 3359.

³⁷ U. S. Pat. 1,254,360, Jan. 22, 1918.

^{37a} Ger. Pat. 290,883, Oct. 23, 1914.

80 per cent purity is obtained. A gas of much higher hydrogen content has been produced by the Berlin-Anhaltischen Maschinenbau A.-G. which is based on investigations made by Bunte. The illuminating gas is first freed of carbon dioxide and is then conducted over white-hot coke which decomposes the hydrocarbons and yields a gas mixture consisting almost entirely of hydrogen, carbon monoxide and nitrogen. The carbon monoxide is removed by treatment with soda lime and the gas then consists largely of hydrogen with only nitrogen as an impurity. The specific gravity is 0.085 to 0.097 and the gas has been found to be well adapted for most technical purposes. The process can be put in opera-

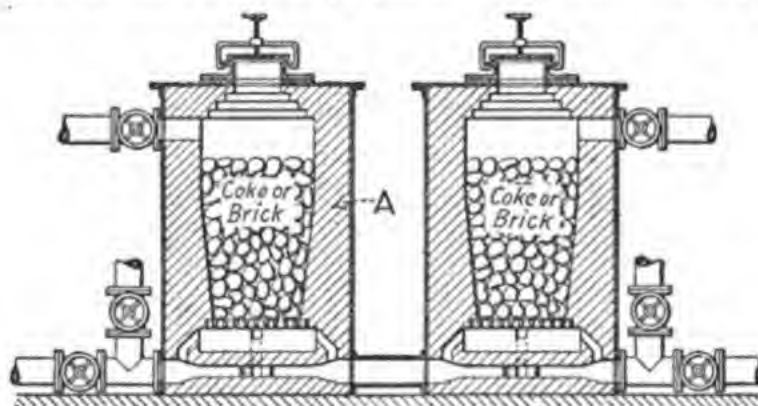


FIG. 181.

tion at any gas works equipped with a water-gas plant and the installation is not very costly.²⁸

5931. In a French process²⁹ coke-oven gas is heated above 1200° C. to decompose the hydrocarbons with production of hydrogen. The decomposition is preferably effected in presence of refractory material which may be impregnated with catalysts.

5931A. Coke-oven, blast-furnace, or lignite-distillation gases containing a proportion of carbon dioxide too high for satisfactory use in reduction are rendered suitable by being passed over coke at a temperature such that in the treated gases the ratio $\text{CO}_2 : \text{CO}$ does not exceed 0.45 and the ratio $\text{CO} : \text{CH}_4$ is at least 1.5. Alternatively, a portion only of the gas is treated and mixed with the remaining gas in proportion such that the mixture conforms to the required standard.^{29a}

5932. We have already seen that in the process of fractionating coke-oven gas, methane is obtained. Battig³⁰ decomposes the methane into carbon and hydrogen by passing it over highly heated coke. This operation may take place in the coke-oven itself.

5933. In an alternative method of carrying out the operation methane is passed over heated brickwork and then against baffle walls on which carbon is deposited. The resulting hydrogen passes, in another chamber, over brickwork giving up its heat. The methane

²⁸ Sander, *Zeitschr. angew. Chem.*, 1912, 2406.

²⁹ Brit. Pat. 296,291, Mar. 3, 1927, to Cie. nat. de mat. color. et manif. de prod. chim. réunies (Etabl. Kuhlmann).

^{29a} Brit. Pat. 298,190, Sept. 24, 1928, to Kali-Ind. A.-G., addn. to 288,154; *Brit. Chem. Abst.*, 1930, 143B.

³⁰ French Pat. 634,711, May 19, 1927; Brit. Pat. 271,491 (convention date, May 20, 1926).

current is stopped and air admitted. Heated by the brickwork the air enters the chamber containing the deposited carbon, which is burned. The hot oxide is made to pass over and give up its heat to brickwork and the cycle is recommenced with methane.²¹

5934. A process for which it is claimed that it yields hydrogen of great purity is described by Burwell.²² It is a mixed process, i.e., it employs both thermal decomposition and reaction with steam. Hydrocarbon material is heated at 1050°–1150° to produce a mixture of hydrogen, carbon monoxide, carbon, and hydrocarbons, from which carbon is removed by settlement and aromatic hydrocarbons by scrubbing with water. Hydrocarbons similar to methane are converted into carbon monoxide by heating the moist mixture at 1230°–1280°, and the carbon monoxide is converted into dioxide by adding excess of oxygen to the dried gases and passing them over a manganese dioxide catalyst below 100°. Any oxygen remaining is removed by passing the gases over heated copper, and carbon dioxide by caustic alkali solution.

5935. Jakowsky²³ describes an apparatus and a process for producing carbon-black and hydrogen, together with unsaturated gases. The invention is chiefly concerned with the economical production of carbon black of fine quality from hydrocarbon oil or from natural gas. This is effected by using a localized source of heat (e.g., a high-voltage arc) and rapidly cooling the product. In the case of oils this combination is secured by passing the oil over an arc plunged in it and allowing the current of relatively cool oil to carry away the suspended carbon. The hydrogen is collected in any convenient manner.

5935A. Hydrogen or a hydrogen-nitrogen mixture is obtained by exposing coke-oven gas or natural gas together with air, oxygen or carbon dioxide, with or without steam, to the action of an electric arc and converting the carbon monoxide formed into hydrogen and carbon dioxide by treatment with steam, then separating the carbon dioxide. The process is so regulated that combustion of the hydrogen content of the materials used takes place only to a slight extent.²⁴

5935B. Coke-oven gases are mixed with a limited supply of steam, e.g., 5–16 per cent by volume for a gas containing 30 per cent methane, and passed through a bed of preheated refractory material. The heat of the gases produced is used to preheat air, and the heat required to bring about interaction of the steam and the hydrocarbons in the gases is obtained by the combustion of the deposited carbon in the preheated air, each reaction period being followed by a reheating period.²⁵

5935C. Methane is blown into molten iron, according to another process for preparing hydrogen. The carbon liberated dissolves in the iron and is subsequently removed by blowing with air.²⁶

5935D. Natural gas can be cracked in a water-gas generator by making alternate air blasts and gas runs. The resultant gas is composed largely of hydrogen, and may be used (a) mixed in small amounts with natural gas in place of the latter, (b) carbureted and mixed in small amounts with natural gas or used straight as manufactured gas for city distribution, (c) mixed with natural and water-gas with varying amounts of blow-run gas and distributed as city gas (this mixed gas can be blended with coal gas in almost all proportions and used in common burners without adjustment), (d) as a source of hydrogen and (e) mixed with water-gas to give a CO : H₂ ratio suitable for methanol. Approximately 7 pounds of carbon black per 1000 cubic feet of gas cracked can be recovered. The amount of solid fuel chargeable to the cracking operation is less when some water-gas is made than when only alternate air blasts and gas runs are used.²⁷

²¹ Brit. Pat. 271,483, May 18, 1927, to Battig; *Brit. Chem. Abst.*, 1928, 748B; cf. Can. Pat. 284,117, Oct. 23, 1928, to Battig; *Chem. Abst.*, 1929, 23, 677; French Pat., 635,670, May 18, 1927, to Battig; *Chem. Abst.*, 1928, 22, 4737; *Chem. Age* (London), 1927, 17, 115. See also U. S. Pat. 1,726,877, to Battig.

²² U. S. Pat. 1,689,858, Oct. 30, 1928, assigned to Alox Chem. Corp.; *Brit. Chem. Abst.*, 1929, 171B.

²³ U. S. Pat. 1,597,277, Aug. 24, 1926.

²⁴ I. G. Farbenind. A.-G., Brit. Pat. 307,529, Dec. 2, 1927; *Chem. Abst.*, 1929, 5282. See also Ger. Pat. 488,502, April 16, 1926, Wietzel, Starke and Eisenhut, inventors; *Chem. Abst.*, 1930, 2251.

²⁵ Tyrer and Imperial Chem. Industries, Ltd., Brit. Pat. 323,864, Nov. 16, 1928; *Brit. Chem. Abst.*, 1930, 312B.

²⁶ Tyrer, Brit. Pat. 328,048, Jan. 25, 1929, to Imperial Chem. Industries, Ltd.; *Brit. Chem. Abst.*, 1930, 613B.

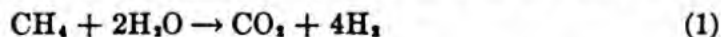
²⁷ Odell, *Bur. Mines, Rept. of Investigations* 2991, 1930; *Chem. Abst.*, 1930, 2577.

HYDROGEN FROM HYDROCARBONS BY INTERACTION WITH STEAM ³⁴

5936. Exothermic hydrocarbons, such as petroleum vapors, mixed with steam may be decomposed with the formation of hydrogen and carbon monoxide; in this case the combination of nascent carbon and oxygen supplies a portion of the heat required by the reaction, the balance which is required to dissociate steam and hydrocarbon being supplied by external heating. By admitting a regulated quantity of oxygen, the combination of the latter with nascent carbon may be made to provide all the heat required by the reaction, it being then only necessary to heat the hydrocarbons initially to their temperature of dissociation.

5936A. Stanley ³⁵ has investigated the reaction between methane and steam at temperatures between 500° and 1000° C., at atmospheric pressure, in presence of various catalysts. The results are:

I. Using equimolecular quantities, low temperatures favor the reaction:



II. While higher temperatures favor:



(2) can be taken almost to completion at 1000° C.

III. Excess of steam favors (1).

5937. Pictet avails himself of this reaction in what he treats as a modification of the process described in paragraph 5902. ³⁶

5937A. External heat (39.36 units for every 18 grams of water) is applied for decomposing the water vapor, in addition to that required to decompose the hydrocarbon vapors, for which the temperature is raised substantially to the melting point of iron. Water and hydrocarbons are fed, for example, into an iron tube, which is of sufficient length (say 3 to 4 meters) to enable the supplementary heat to be imparted without damage, and these being vaporized on entry, react in the further end of the tube, which is the more strongly heated; the gas produced is then cooled and passes through a filter to a gas holder, there being a soot chamber and also arrangements for the removal of soot from the tube and filter. Ten liters of petroleum, mixed with 3 to 5.5 liters of water, may be thus decomposed per hour, in the apparatus described, the mixture furnishing approximately 3000 liters of gas for every liter of hydrocarbon, with calorific value of 3000 to 3600 heat units per cubic meter. By regulating the supply of water, any desired proportion of carbon can be converted into carbon monoxide.

In preparing hydrogen from crude petroleum or petroleum tar oils, the vapors are heated in such a manner that 18.1 calories are supplied to 16 grams of gas, with a tube temperature of 1200° to 1350° C. ³⁷

5938. Partial Combustion. Some of the methods for obtaining hydrogen from hydrocarbons depend on incomplete combustion. While these processes should logically be separated from those using the reaction with steam, it is con-

³⁴ This method of obtaining hydrogen being specially adapted to the working up of the berginization residual gases has been much developed in that connection; see Chap. XLVI.

³⁵ *Report on the Work of the Dept. of Oil Ref. and Eng'g., Univ. of Birmingham, 1926-1928, 13.*

³⁶ Brit. Pat. 14,703, June 21, 1911.

³⁷ Brit. Pat. 13,397, June 3, 1911. Geisenberger (see para. 5904) mentions steam treatment as an alternative to straight thermal decomposition.

venient to consider them here. In fact, the two methods are often combined, or prescribed as alternatives.

5939. Patart ³⁸ obtains a suitable mixture for the catalytic synthesis of methanol by incomplete combustion of methane. The methane, mixed with half its volume of oxygen is injected into coke maintained at 1000° C.

5940. Brownlee and Uhlinger ³⁹ employ a method of obtaining carbon monoxide, hydrogen and nitrogen from the products of combustion of internal combustion engines.

Natural gas, coal gas, or other suitable gaseous, liquid or solid carbonaceous substance, is mixed with an amount of air not sufficient for complete combustion, and the mixture is exploded in the cylinder of an internal combustion engine. The mixture is so regulated that the proportion of air is such as to yield the largest practicable quantities of carbon monoxide and hydrogen. For example, if natural gas is used, a mixture of approximately 1 volume of gas to 6½ volumes of air is preferably employed with a compression before explosion of 70 to 80 lb. Under these conditions considerable power is produced and at the same time good yields of carbon monoxide and hydrogen are obtained. The mixture of water vapor, carbon dioxide, carbon monoxide, hydrogen and nitrogen resulting after the combustion or explosion is cooled to remove the moisture, then compressed, and the carbon dioxide, carbon monoxide and nitrogen liquefied in turn, thus leaving hydrogen in the gaseous state, but highly compressed. Instead of compressing and liquefying the carbon dioxide, etc., after the removal of moisture by cooling, this gas may be absorbed with suitable absorbents, as calcium hydroxide, and the carbon monoxide may be withdrawn by ammoniacal cuprous chloride solution, leaving the nitrogen and hydrogen to be separated by compression and liquefaction of the nitrogen. In place of air, nearly pure oxygen may be used.⁴⁰ A mixture of equal volumes of natural gas and oxygen may be employed under a compression of 70 to 80 lb. From 1000 cu. ft. of Pennsylvania natural gas 1300 to 1350 cu. ft. of hydrogen will be obtained.

5940A. In a process for the continuous production of water-gas and hydrogen, gaseous hydrocarbons are incompletely burnt with air or oxygen, and the resulting gases are freed from water vapor and carbon dioxide.^{40a}

5940B. Residual gases from the manufacture of hydrogen from coke-oven gases are partly burnt by passing them with insufficient air through a gas producer filled with refractory material at a high temperature. Saturated hydrocarbons are removed by catalytic destruction in the presence of iron, nickel or chromium, and carbon dioxide by washing with ammonia.^{40b}

5941. Battig subjects the methane fraction ⁴¹ resulting from the liquefaction process of purifying coke-oven gas to the action of oxygen or steam, or both, to convert the methane into carbon dioxide and hydrogen. The carbon dioxide is removed by pressure water washing, the water by cooling to -70° C. The hydrogen is then purified by the methods described under Liquefaction.⁴²

5941A. Fuel with the usual amount of volatile constituents is gasified, without previous coking, in a mixture of oxygen (and/or air) and water vapor so that the nitrogen content of the resulting gas is not greater than that required for ammonia synthesis; the hydrocarbons are converted by oxygen or oxygen and water vapor into carbon monoxide and hydrogen.^{42a}

5941B. To make gas which has a high calorific value and which is rich in hydrogen and

³⁸ Brit. Pat. 247,176, 1925; Can. Pat. 264,600, Sept. 28, 1926.

³⁹ U. S. Pat. 1,107,581, Aug. 18, 1914.

⁴⁰ U. S. Pat. 1,107,582, Aug. 18, 1914.

^{40a} French Pat. 630,327, Mar. 5, 1927, to Soc. Internat. des Combustibles Liquides, from Deuts. Bergin-A.-G. f. Kohle- u. Erdölchemie; *Brit. Chem. Abst.*, 1930, 92B.

^{40b} Compagnie de Bethune, French Pat. 670,878, June 27, 1928; *Chem. Abst.*, 1930, 1942.

⁴¹ Cf. para. 5932.

⁴² Brit. Pat. 294,113, July 16, 1927; *Chem. Abst.*, 1929, 23, 1999.

^{42a} Gross, Brit. Pat. 289,080, Mar. 15, 1928; *Brit. Chem. Abst.*, 1929, 841B.

carbon monoxide, pulverulent solid fuel is gasified in a continuous process with the aid of a gas containing a higher percentage of free oxygen than atmospheric air.^{42b}

5942. All three methods, thermal decomposition, partial combustion, steam treatment, have been combined in one process.⁴³ Mixtures of air, oxygen, or carbon dioxide, and steam, if desired, with gaseous, liquid, or solid carbonaceous material, e.g., methane, gases obtained in the distillation of coal, tars, oils, etc., but excluding products obtained in the conversion of saturated into unsaturated hydrocarbons are subjected to the action of the electric arc, and the gas mixtures obtained are treated with steam to convert carbon monoxide into carbon dioxide and hydrogen, the carbon dioxide and other impurities being removed from the product. A mixture of nitrogen and hydrogen suitable for the synthesis of ammonia is obtained by using air as the oxidizing gas, and subsequently adding hydrogen prepared, e.g., by a similar process using carbon dioxide instead of air, to adjust the mixture to the correct proportion.

5942A. In a process of hydrogen regeneration^{42a} a mixture of hydrocarbons and water vapor is decomposed by the action of heat into hydrogen and carbon monoxide. The highly heated gases obtained from the decomposition are cooled by contact with cold water. The water thus heated is brought into direct contact with fresh gases containing hydrocarbons to be subjected to the reaction, thus heating the gases and charging them with water vapor. The resulting gas mixture is then introduced into the decomposition chamber, where carbon monoxide and hydrogen are produced. If pure hydrogen is desired, the gas issuing from the decomposition chamber is passed, with further additions of steam or water, over a suitable catalyst, preferably at a lower temperature, and the carbon monoxide and carbon dioxide are eliminated.^{42b}

5943. Casale⁴⁴ treats hydrocarbon vapor in a combustion chamber, with steam and oxygen. Carbon monoxide and hydrogen are produced and, by further treatment with steam, the monoxide is converted into dioxide. The oxygen is obtained from liquid air, the nitrogen being added to the hydrogen produced, to form a mixture for ammonia synthesis.

5944. Many of the processes for obtaining hydrogen from hydrocarbons by interaction with steam, or by incomplete combustion or by a combination of methods, use catalysts to accelerate the reaction or to cause it to take place at lower temperatures.

5945. Conversion of Methane into Hydrogen and Carbon Monoxide. Fischer and Tropsch⁴⁵ investigated this reaction with mixtures of methane and

^{42a} Wietzel (to I. G. Farbenind. A.-G.), U. S. Pat. 1,751,117, March 18, 1930; *Chem. Abst.*, 1930, 2583.

⁴³ Brit. Pat. 307,529, Dec. 2, 1927, to Johnson (from I. G. Farbenind. A.-G.); *Brit. Chem. Abst.*, 1929, 393B. By one procedure methane is treated with steam in proportions and under conditions such that the issuing gases contain 2-15 per cent (preferably 4-5 per cent) of unchanged methane, which is subsequently removed, e.g., by combustion with oxygen or, together with carbon dioxide, by extraction with solvents (gasoline) under pressure. Removal of carbon monoxide from the products may be facilitated by converting, prior to the removal of undesired gases, the greater part of it into carbon dioxide and hydrogen by the action of steam and the remainder catalytically into methane. I. G. Farbenind. A.-G., Brit. Pat. 319,957, Oct. 18, 1928; *Brit. Chem. Abst.*, 1929, 1014B.

^{42b} Brit. Pat. 265,989, Nov. 2, 1927, to I. G. Farbenind. A.-G.

⁴⁴ *Brit. Chem. Abst.*, 1927, 900B.

⁴⁵ Can. Pat. 285,619, Dec. 18, 1928; Austr. Pat. 111,555, July 15, 1928.

⁴⁶ *Brennstoff-Chem.*, 1928, 9, 39; *Chem. Abst.*, 1928, 22, 1952.

carbon dioxide, methane and coke-oven gas, and coke-oven gas with water vapor over various catalysts (iron, cobalt, nickel, copper, molybdenum and tungsten) supported on clay, silica and magnesium carbonate or mixed with alumina. Temperatures from 840° C. to 920° C. were used with various space-time velocities. For oven gas-steam mixtures the best S. T. V. was 800 cc. gas per hour, per cc. catalyst. No conditions gave complete decomposition of methane. Nickel and cobalt were the best catalysts and *cobalt was equal to nickel*. Iron, copper, molybdenum and tungsten were poor catalysts. The addition of alumina increased the activity of nickel and cobalt. Clay proved the best carrier.

5945A. The catalytic oxidation of methane to hydrogen and carbon monoxide or dioxide in the presence of nickel can be promoted by various metallic oxides, alumina giving the best yield in the latter case and magnesia in the former.⁴⁶

5945B. Catalysts for use in the thermal decomposition of hydrocarbons, alone, or mixed with steam, air, etc., comprise nickel, cobalt, or iron mixed with aluminum compounds which contain oxygen and at least one of the elements silicon, hydrogen, carbon, boron, phosphorus, and sulphur, and which are not decomposed during the reaction (for example, kaolin)⁴⁶.

5946. Mittasch and Schneider ⁴⁶ pass hydrocarbons and steam over a nickel catalyzer distributed on a carrier at a temperature of somewhat above 700° C. and produce hydrogen and carbon monoxide or carbon dioxide.⁴⁷

5947. They state that the conversion of hydrocarbons and steam into hydrogen and carbon monoxide or carbon dioxide can be carried out rapidly and completely by employing a nickel catalytic agent distributed on a fireproof carrier and by working at a temperature above 700° C. Mittasch and Schneider observe that during the reaction it is possible that the nickel is converted into an oxide of nickel; or vice versa, it is also possible that the oxide or other compound of nickel is reduced to the metallic form or to a compound containing carbon, so that it is equivalent whether metallic nickel or nickel oxide or other suitable compound be taken at the commencement of the reaction. Such carriers are employed as do not react with nickel oxide under the conditions obtaining during the reaction, since the contact mass, it is claimed, then retains its activity even after being employed for a long time.

When working according to this process, a gas mixture free from or containing only small quantities of hydrocarbons results and after removal of the carbon monoxide and carbon dioxide hydrogen remains which Mittasch and Schneider note is suitable for the catalytic production of ammonia, or for reducing fats.

5948. The process is carried out in upright furnaces or tubes lined with fireproof material. The necessary heat can be applied internally, by burning hydrocarbons in the reaction space, and this heating can be carried on before or during the actual production of hydrogen. It is particularly advantageous to pass alternately mixtures of hydrocarbon or other fuel and air, and hydrocarbon and steam, into the reaction space, since by this means it is easy to maintain the requisite temperature. The heat contained in the gases leaving the reaction space can be used to preheat the gas mixture about to enter the furnace. The gas mixture obtained, in so far as it contains carbon monoxide, if necessary after adding a further quantity of steam, can be passed over a contact agent, in order to convert the carbon monoxide into carbon dioxide.

5949. The following procedure will serve to illustrate the process: Magnesia in the form of lumps is burnt at a high temperature. The lumps are soaked with a solution of nickel nitrate so that the magnesia contains from about 2 to 5 per cent of nickel, and then, after

⁴⁶ Kubota and Yamanaka, *Bull. Chem. Soc. Japan*, 1929, 4, 211-20; *Brit. Chem. Abst.*, 1930, 43A.

⁴⁶ *Brit. Pat.* 323,855, Nov. 8, 1928, to I. G.; *Brit. Chem. Abst.*, 1930, 231B.

⁴⁶ U. S. Pat. 1,128,804, Feb. 16, 1915.

⁴⁷ See French Pat. 463,114, of 1913; *J.S.C.I.*, 1914, 313; also *Brit. Pat.* 12,978, June 4, 1913.

heating to decompose the nitrate, the product is placed in a contact furnace and a mixture containing methane and steam is passed over it at from 800° to 1000° C. The reaction takes place rapidly and the activity of the catalytic agent does not diminish. Another method of producing a catalyst of this character, recommended by Mittasch and Schneider, consists in precipitating metallic nickel on a carrier by the decomposition of nickel carbonyl.

5950. Instead of gaseous hydrocarbons, either liquid or solid hydrocarbons can be used, in which case the latter are first vaporized or are injected directly into the reaction space, or the pipes leading to the reaction space. Further, mixtures containing hydrocarbons can be employed, such as coal gas. The nickel also can be used in admixture with other metals or metallic oxides.

5951. Hydrocarbons (methane, ethane, ethylene, or benzene) are treated with steam in the presence of iron, nickel, or cobalt, activated by the addition of metals whose oxides are reducible with difficulty, such as chromium, vanadium, and compounds of alkali, alkaline earth, and earth metals. A temperature of 300°–650° C. may be employed, and the hydrocarbons are converted into carbon dioxide and hydrogen, without formation of carbon monoxide. The carbon dioxide is removed, and the hydrogen employed for the synthesis of ammonia or methyl alcohol, or for hydrogenation of coal, tars, oils, etc.⁴⁸

5952. Hydrogen Regeneration.⁴⁹ In the recovery of hydrogen from methane, ethane and the like, present in the residual gases of berginization, these gases are mixed with carbon dioxide (with or without steam) and passed over a heated refractory catalyst contained in a shaft furnace; alternatively, the furnace may be filled with coke and worked as a producer, the gas being introduced at the cold blowing stage. The following is an example of the process: residual gas from berginization containing 30–40 per cent of methane is mixed with carbon dioxide, etc., to obtain a mixture of carbon dioxide 23.6 per cent, hydrogen 52 per cent, methane 22.5 per cent, nitrogen 1.3 per cent and carbon monoxide 0.6 per cent. This mixture is passed through a shaft furnace heated to 1100° C. having a refractory filling containing a nickel catalyst. The percentage composition of the issuing gas is carbon monoxide 31.4, hydrogen 66.2, carbon dioxide 1.1, nitrogen, etc., 1.3. By the usual steam treatment at 500° C. the monoxide may be converted into dioxide and removed.⁵⁰

5953. Hydrocarbons are partially burned by means of oxygen or air enriched with oxygen, possibly with the addition of water vapor, and the resulting gases treated with activated catalysts which facilitate the conversion of a mixture of hydrocarbons, carbon monoxide, and steam into a mixture containing hydrogen and carbon monoxide or dioxide. When carbon

⁴⁸ Brit. Pat. 267,535 (convention date, Mar. 10, 1926), to I. G. Farbenind. A.-G.; *Chem. Age* (London), 1927, **17**, 487. In the production of hydrogen from methane or gases containing it, by means of steam in the presence of a catalyst, it is found to be preferable to regulate the amount of steam and rate of flow of gas so that 2–15 per cent of methane still remains in the gas. The residual methane is then removed by washing with solvents under pressure, or by decomposition with air. By this incomplete decomposition it is possible to operate at a temperature about 100° C. lower than usual. When the residual methane is removed by washing, the greater part of the carbon monoxide is converted into carbon dioxide by means of steam and the gaseous mixture then treated with gasoline fractions boiling between 150°–200° C. in a washing tower. The carbon dioxide and methane are washed out together, and any residual carbon monoxide is removed by washing with a solution of a copper salt. The lower temperature which may be employed in this process is less deleterious to the apparatus, which may be of alloy steels such as "Nicrotherm," "WT2," or "V2A." Brit. Pat. appln. 319,957, appln. date Oct. 18, 1928, I. G. Farbenind. A.-G.; *Chem. Age* (London) **1929**, 453.

⁴⁹ I. G. Brit. Pat. 279,072, convention date, Oct. 14, 1926.

⁵⁰ *Chem. Age* (London), 1927, **17**, 557. Cf. French Pat. 34,048, Sept. 13, 1927, addn. to 617,504, to I. G.; *Chem. Abst.*, **1929**, 4802.

monoxide is not desired in the product, steam is added during the second stage and suitable catalysts are used to give a mixture of hydrogen and carbon dioxide, the latter being finally removed, if desired. More than one catalyst may be employed; e.g., the preheated gases may first meet a heat-resisting catalyst and then a more active catalyst. The partial combustion may be effected by means of flame or by surface combustion, with employment of solid materials upon which catalysts may be deposited. The temperature of the partial combustion is reduced by freeing the hydrocarbons from organic and inorganic sulphur compounds. Instead of subjecting the whole of the gases to partial combustion, a portion may be burned and the products mixed with the remaining hydrocarbons. Thermal decomposition may be employed in the first stage of the process instead of partial combustion. The hydrocarbons may be passed through externally heated tubes and the resulting carbon collected; or, in a discontinuous process, the gases are passed in contact with hot fireproof materials, which are reheated at a subsequent stage by burning the deposited carbon. The decomposition may be facilitated by adding carbon dioxide, oxygen, or steam.⁵¹

5954. The carbon dioxide may be removed in steps. Thus mixtures of methane, etc., with steam are passed successively over a catalyst and material capable of absorbing the carbon dioxide formed, e.g., calcium or cerous oxide, at a temperature sufficiently high to prevent condensation of water, the process being repeated if necessary. The oxide is subsequently regenerated by heating the carbonate.⁵¹ When using nickel as catalyst and cerous oxide as absorbent of carbon dioxide the separation of carbon dioxide takes place at temperatures high enough to prevent condensation of water. The quantity of steam used is five to seven times the theoretical quantity. This method of working gives almost quantitative conversion at 400°–600° C.

5955. The catalyst for the process just described contains at least one metal (or compound) from the iron group and at least one other metal or metal compound, preferably a metal forming a difficultly reducible oxide. Thus, a mixture of nickel, manganese, and aluminum nitrate solutions is precipitated with potassium carbonate solution. The precipitate is washed with potassium nitrate solution, dried and reduced in hydrogen at 350° C. Over this methane (1 vol.) and steam (6.2 vols.) are passed at 430°–650° C.⁵²

5956. According to Casale⁵⁴ the purity of the hydrogen obtained by treatment of gaseous hydrocarbons such as methane is increased by working at pressures below atmospheric. A mixture of methane and oxygen with steam heated to 1100°–1300° C. (the temperature being regulated by admission of oxygen) under reduced pressure yields a mixture of hydrogen and carbon oxides which may be used directly for the methanol synthesis.

5957. The waste gases obtained in the hydrogenation of coal at high pressures, and which contain methane and some hydrogen, are treated with steam at different temperatures to obtain gases rich in hydrogen for use again in the hydrogenation process. By treating with steam at high temperature, the methane is converted into hydrogen and carbon monoxide, and the carbon monoxide is

⁵¹ Brit. Pat. 288,662, Nov. 15, 1926, to Johnson (an I. G. communication), compare Ger. Pat. 403,049. A process bearing a general resemblance to this is described in Brit. Pat. 254,713, July 2, 1925, to the I. G. The catalysts mentioned are nickel on magnesia, iron alloys, molten iron; *Chem. Abst.*, 1927, **21**, 2792.

⁵² Brit. Pat. 291,244, June 18, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abst.*, 1928, 523B; *Chem. Age* (London), 1928, **18**, 614.

⁵³ Swiss Pat. 127,030, Mar. 8, 1927, to I. G.; *Chem. Abst.* 1929, **23**, 1225.

⁵⁴ Brit. Pat. 274,610, June 2, 1926; *Chem. Age* (London), 1927, **17**, 199. U. S. Pat. 1,734,559, Nov. 5, 1929; *Chem. Abst.*, 1930, 471.

then converted catalytically into hydrogen and carbon dioxide, the latter being removed. The process can be applied to the preparation of gases rich in hydrogen from coke-oven gases. The gases from a hydrogenation chamber pass through a condenser, a liquid separator and devices for removing benzene and sulphureted hydrogen. Steam is admitted and the gases pass to a regeneratively superheated apparatus where the first-mentioned reaction is effected. Steam or water is again admitted, and the gases pass to a chamber containing an iron oxide catalyst. The gases finally pass to a cooler, pump and scrubber, where carbon dioxide is removed, and then are pumped to the hydrogenation chamber.⁵⁶

5958. When producing hydrogen from a hydrocarbon mixture by passing the latter with steam over a catalyst at a temperature below 700° C.⁵⁶, Williams⁵⁷ found that the presence of unsaturated hydrocarbons caused the deposit of carbon in and on the catalyst mass. He meets this difficulty by subjecting the gas to catalytic hydrogenation before or during the steam treatment. For this purpose hydrogen is added to the mixture.

5959. In connection with Williams' catalytic steam-hydrocarbon process, to which reference is made in the preceding paragraph, Beekley⁵⁸ states that it is necessary to supply heat to maintain the catalyst at the desired temperature. This may be effected by the addition of oxygen, but sudden and complete inactivation of the catalyst sometimes attends the adoption of this method. Beekley, therefore, prescribes the addition, with the oxygen, of an equivalent quantity of a reducing gas, such as purified water-gas.

5959A. A mixture of steam and methane is passed over a succession of spaced catalyst bodies (such as nickel and a promoter) and oxygen is added to the gaseous mixture during its passage through the space between the catalyst bodies in the proportion required to maintain the temperature necessary for the reaction by combustion of some of the hydrocarbon.⁵⁹

5960. Blake⁶⁰ causes methane to react with steam in presence of a catalyst at a temperature between 400° and 700° C, and with a volume ratio of steam to methane⁶⁰ within the range 3.5 : 1 to 44 : 1 and at substantially a minimum value for the temperature employed and for a predetermined methane conversion and carbon monoxide content of the resulting gas. Blake's curves, from which the ratio steam : methane can be determined, are reproduced in Figs. 182 and 183. As a guide to the method of using these curves, suppose a methane

⁵⁶ *Chem. Age* (London), 1926, 14, 349; Brit. Pats. to Bergius, 244,730, convention date Dec. 18, 1924, and 216,882, May 28, 1924, to Internat. Bergin-Comp.; U. S. Pat. 1,699,177, Jan. 15, 1929, to Bergius. Can. Pat. 263,477, Aug. 17, 1926.

⁵⁷ This is the process covered by Williams' Application Serial No. 118,600, to which reference is made in the patent now under consideration. This application of Williams is also mentioned in U. S. Pat. 1,713,325 to Blake (see para. 5960), where the catalyst used by Williams is said to be a suitably promoted nickel catalyst, such as nickel chromate, or nickel promoted with ceria and alumina.

⁵⁸ U. S. Pat. 1,673,032, June 12, 1928, assigned to Lazote, Inc.

⁵⁹ U. S. Pat. 1,711,036, Apr. 30, 1929, assigned to Lazote, Inc.

⁶⁰ U. S. Pat. 1,736,065, Nov. 19, 1929, to Williams, to DuPont Ammonia Corp; *Chem. Abst.*, 1930, 697.

⁶¹ U. S. Pat. 1,713,325, May 14, 1929, assigned to Lazote, Inc.; see footnote 56.

⁶² Cf. paras. 5954 and 5955.

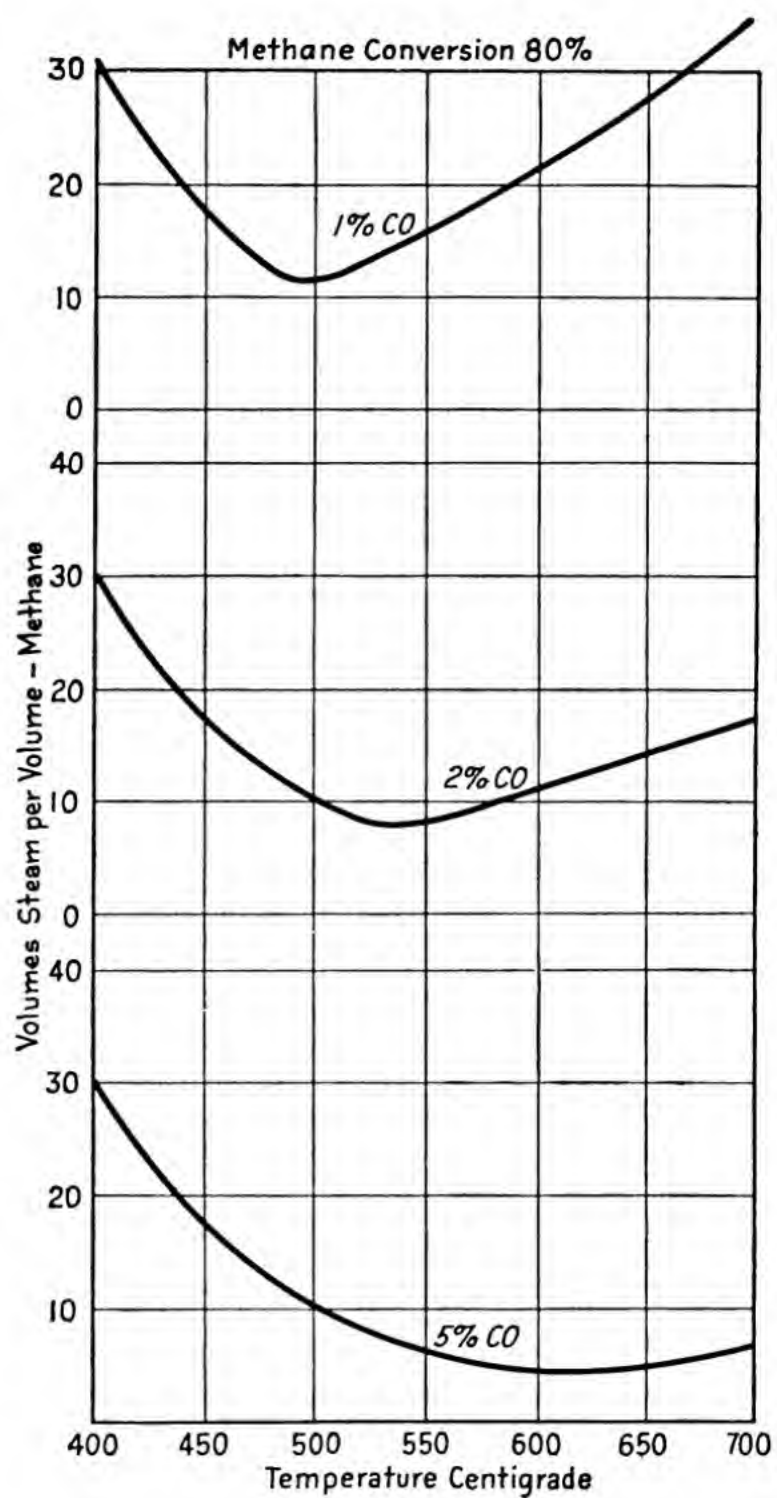


FIG. 182.

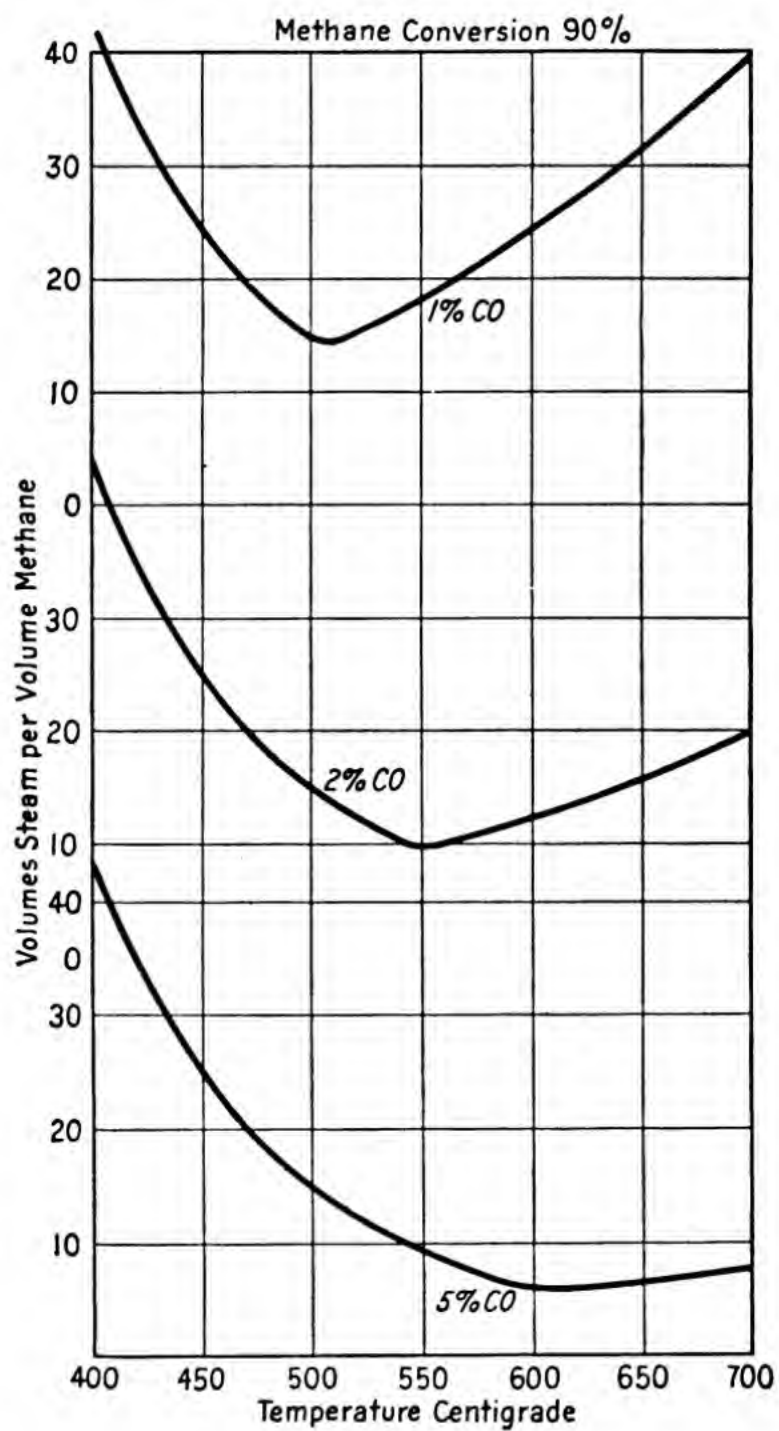


FIG. 183.

conversion of 80 per cent (Fig. 182) and a requirement of 1 per cent carbon monoxide: the uppermost curve shows that the steam: methane ratio is lowest (between 12 and 14) at about 495° C. With 2 per cent carbon monoxide (middle curve) the minimum ratio is 8 at 450° C.

5961. A method of obtaining unsaturated hydrocarbons from saturated, and of using the residual gases for the production of carbon monoxide and hydrogen and ultimately of hydrogen only also has been described. The latter is almost certainly the main object, since it serves to supply hydrogen for berginization and allied processes. Dehydrogenation of the saturated hydrocarbons, accompanied by cracking, is effected either by heating in an arc or by incomplete combustion. *Examples:* (1) Methane containing some hydrogen is passed through an electric arc and acetylene absorbed from the product by active charcoal: the residual gases are then heated to 1100° C. by preheating and partial combustion, and passed, with steam, over a nickel-alumina catalyst to convert them into a mixture of hydrogen and carbon oxides: (2) Natural gas is subjected to partial combustion to produce acetylene and the gas is passed over silica coated with graphite to form benzene which is absorbed in active charcoal: the residual gases, subjected to partial combustion, are mixed with steam and passed over a nickel-magnesia catalyst, whereby is produced a hydrogen-carbon monoxide mixture.⁶¹

5962. The yield of hydrogen and carbon monoxide, in processes of the kind described in the preceding paragraph, is increased if care be taken to remove not only the inorganic but also the organically combined sulphur from the gases. This may be effected by passing the latter over a metallic mass which will fix the sulphur compounds or convert them into hydrogen sulphide.⁶²

5963. Gas mixtures rich in hydrogen are obtained by passing distillation gases, hydrocarbons or gaseous mixtures containing hydrocarbons over catalysts (such as iron, cobalt, nickel, chromium, aluminum, manganese, silicon, carbon, copper, vanadium, tungsten and compounds or mixed crystals of these elements), in admixture with superheated steam at temperatures of 1000° or higher. The passage of coke-oven gas together with superheated steam at 1100° over a catalyst comprising chromium and aluminum results in a product composed almost entirely of hydrogen, nitrogen and carbon monoxide. A conduit of carborundum may be used for the reaction and when so used it also has the effect of a catalyst.⁶³

5964. In the production of hydrogen from methane and steam with catalysts, the reaction is carried out so that the reaction gases contain from 2 to 15 per cent of methane which is then eliminated.⁶⁴

⁶¹ Brit. Pat. 269,547, (convention date, Apr. 15, 1926) to I. G. Chem. Age (London), 1927, 16, 605.

⁶² French Pat. to I. G., 644,147, Nov. 18, 1927; *Chem. Abst.*, 1929, 23, 1728.

⁶³ Schulz and Eisenstecken (to Vereinigte Stahlwerke A.-G.), Brit. Pat. 314,870, July 3, 1928; *Chem. Abst.*, 1930, 1475-6.

⁶⁴ French Pat. 672, 935, April 11, 1927, to the I. G.; *Chem. Abst.*, 1930, 2254.

CHAPTER LX

HYDROGEN BY THE ELECTROLYSIS OF WATER

6000. The production of hydrogen and oxygen by the electrolysis of water, though one of the oldest electrochemical experiments, and proposed in a large number of patents was, for a long period, carried out industrially only to a limited extent. There was considerable difficulty in developing the laboratory apparatus so that it would operate successfully in practice, one of the hardest conditions to meet being the necessity of absolute safety of operation, and this required the exclusion of every possibility of the formation of an explosive gas mixture. Another difficult matter was the requirement of providing a material for the electrodes, which was not at all or only slightly attacked by the electrolyte, and the necessity of constructing apparatus with a small internal resistance. One by one these problems were solved. The welding industry needed oxygen in quantity; engineers and chemists engaged in the expansion of the infant industry of oil hardening became interested in methods of deriving hydrogen by electrolysis. A period of development followed which eventually brought forth simple and reliable electrolytic equipment especially suited for locations where both oxygen and hydrogen were demanded.

6001. In the electrolysis of water there are certain constants whose values are the same under all conditions of operation within certain limits. The *first* constant is the amount of hydrogen liberated per ampere hour of current passed through the cell generator; the figure is 0.03738 g. or 0.014825 cu. ft. of hydrogen gas measured at 0 deg. and 760 mm. pressure. Thus, at 400 amperes, which is the customary operating amperage for most cell generators, the production will be 5.93 cu. ft. of hydrogen and 2.96 cu. ft. of oxygen (at 0 deg. and 760 mm. pressure) per hour. At 20 deg. and 760 mm. pressure the output will be 6.36 cu. ft. of hydrogen and 3.18 cu. ft. of oxygen per hour per cell generator. The *second* constant is the minimum voltage that will force the current through the cell generators. For a solution of sodium hydroxide in water the minimum voltage is 1.69 volts, for potassium hydroxide 1.67 volts; this, then, is the lowest voltage at which decomposition of water, or electrolysis, takes place. In order to produce gas with current at this voltage, the cell generator would have to be constructed in such a manner as to do away with all internal electrical resistance which is obviously impossible and so the operative or practical voltage is higher than the theoretical. With a current of 400 amperes the voltage will vary from 1.9 to 4, depending on the type of cell generator. With the first constant given the amount of hydrogen produced per 400 amperes per hour and the

minimum or theoretical voltage given it is a simple matter to determine the yield of gas per kilowatt-hour of electricity used. The theoretical efficiency will be $400 \text{ amperes} \times 1.69 \text{ volts}$ or 0.676 kilowatt-hour to produce 6.36 cu. ft. of hydrogen. The theoretical yield per kilowatt-hour per cell generator will be 9.408 cu. ft. of hydrogen. In practice the yield is from 4.5 to 8.25 cu. ft. of hydrogen per kilowatt-hour.

6002. In general, electrolytic plants consist of the following important parts, cell generators for producing the gases, a motor-generator set to deliver a direct current at the proper potential or voltage, gasometers and storage tanks for storing the gas as it is generated and compressors and compressor motors for raising the pressure of the gas to the required point. Stripped of everything but essentials the component parts of all cell generators are: a container tank for holding the solution; one or more positive electrodes, one or more negative electrodes, immersed in the solution; means for separating the electrodes to prevent mixture of gas and means for separately collecting each gas as it is generated. The separating medium is usually a diaphragm and may be of metal, earthenware or cloth. The diaphragm may be a conductor or non-conductor of electricity and if of conductive material it should be insulated from the electrodes. The effect of the diaphragm is to divide the generator into two or more partitions, and the gases as generated will rise to the top of the partition, there to be drawn off by means of pipes which lead to header pipes connecting a line of cell generators, each gas, of course, being drawn off by means of separate pipe lines. The header pipes in turn are connected to a main gas line which leads the gases to their respective gasometers. From the gasometers the gas is drawn off by means of compressors and compressed into storage tanks for use.

6003. The majority of installations require a motor-generator set to obtain the required voltage for operating. The current must be direct. The motor-generator set should be heavily built in order to operate on a twenty-four hour load. The compressors employed are specially adapted for handling these gases. The size and character of the gasometers used, of course, depends on the size of the installation.

6004. When reviewing different processes of making hydrogen for the purpose of selecting one adapted to a particular local requirement the cost of electric power for the operation of electrolytic cells is usually the chief factor involved in the consideration of the methods described in the present chapter. While labor costs are low depreciation charges are rather high. There is also the relatively small item of distilled water supplied to the cells to replace water undergoing electrolysis. About 6 gal. of water are required to produce 1000 cu. ft. of hydrogen.

6005. D'Arsonval, in 1885, was perhaps the first to install a plant for furnishing oxygen electrically in the laboratory. He used 30 per cent caustic soda solution as electrolyte, cylindrical sheet-iron electrodes, a current density of 2 amperes per square decimeter, and enclosed the anode in a woolen bag, to serve as a diaphragm. Only the oxygen was saved. The apparatus used sixty amperes, furnished some 100 to 150 liters of oxygen daily, and was in use several years.

6006. Latchinoff used an asbestos cloth partition, 10 per cent caustic soda

solution, iron electrodes, 3.5 amperes per square decimeter and 2.5 volts working tension; or with a 5 to 15 per cent sulfuric acid solution he used lead anodes and carbon cathodes. In his first apparatus, Figs. 184 and 185, the units were all in parallel, but afterwards he used series electrodes, the one side of an electrode acting as an anode and the other as a cathode; a series of forty was used on a normal lighting circuit, with current density of 10 amperes per square decimeter, and

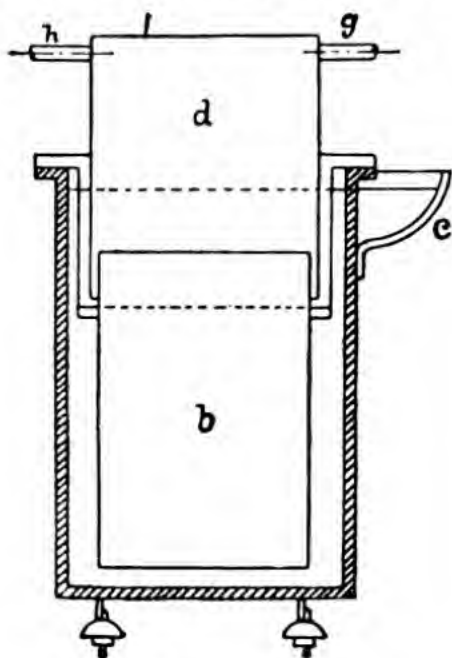


FIG. 184.

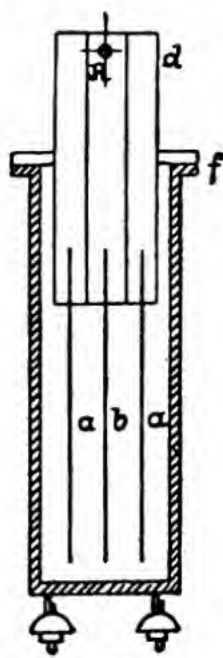


FIG. 185.

parchment partitions between the electrodes to separate the gases. Latchinoff was also the first to carry out the decomposition under pressure, using a strong iron vessel as electrolyzer, and by an ingenious system of floating valves keeping the pressure of the two gases equal in the apparatus. Fig. 186 shows this apparatus, the action of which will be evident from a short inspection.¹

6007. Garuti, in 1892, introduced a new electrolytic principle into the apparatus for the decomposition of water. He used a nearly complete metallic partition between the electrodes, and avoided the evolution of gases on this partition by keeping the working voltage between the electrodes below 3 volts. A metallic partition can only act as an intermediate or bipolar electrode by virtue of the current entering and leaving it; but this would make two decompositions between the original electrodes, necessitating an absorption of $2 \times 1.5 = 3$ volts in decomposition. As long as the working voltage is kept below 3, the partition must act merely as a *partition*, the same as a non-conducting diaphragm.

¹ This apparatus allowed of pressures up to 120 atmospheres. (Taylor, *Industrial Hydrogen*, 1921, p. 108.) For recent developments in the production of electrolytic hydrogen under pressure, see para. 6069.)

Reference to Figs. 187, 188 and 189 will make this entirely clear. If 2 electrodes are placed in a vessel (Fig. 187) containing acidulated water and are separated

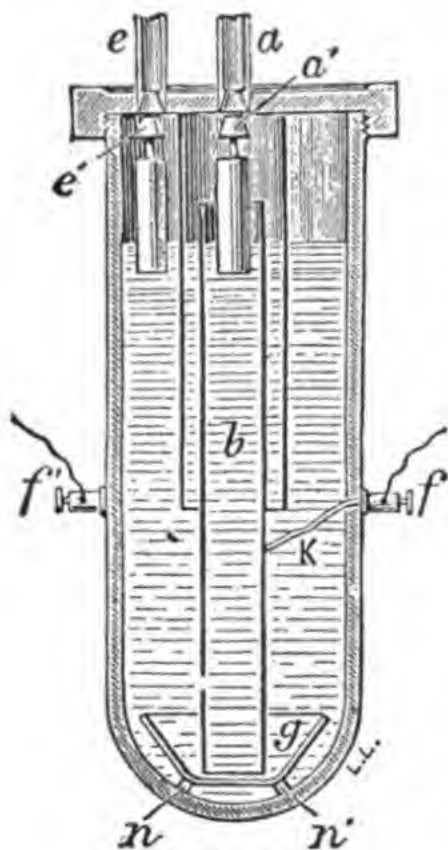


FIG. 186.

partition with small perforations in it, the latter allowing free passage of current but being too small to allow any gas bubbles to pass. The alternate

by a sheet of metal *c* (Fig. 188), two separate decomposition chambers result and the sheet metal serves as a bipolar electrode, so that the side towards the anode evolves hydrogen and that towards the cathode, oxygen. Since the 1.5 volts are required for the decomposition of water, the cells *M* and *N* will require 3 volts. If the diaphragm is raised somewhat so the chambers *M* and *N* are in communication (Fig. 189) the evolution of gas will take place only on the terminal electrodes and not on the intermediate conducting septum. The latter becomes a bipolar electrode only when the electromotive force exceeds 3 volts. The advantage gained by the Garuti process is in the simplicity and economy of making the partitions of sheet metal instead of burnt clay, rubber, glass, etc.

6008. Garuti devised many modifications in the details of his cells, of which Fig. 190 is representative. The original forms made of sheet lead (using dilute sulphuric acid electrolyte) got out of shape too easily, and were replaced by sheet-iron apparatus, using caustic soda solution. The electrodes are only 12 millimeters from each other, and separated by a sheet-iron

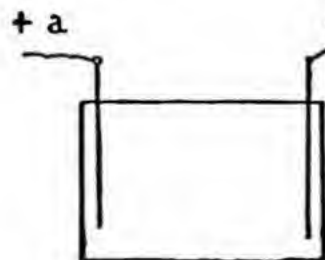


FIG. 187.

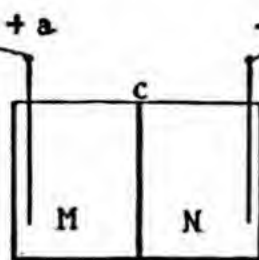


FIG. 188.

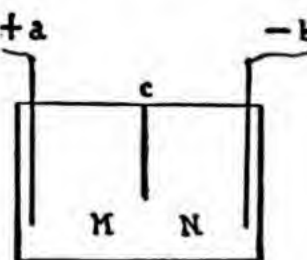


FIG. 189.

compartments are connected with oxygen and hydrogen mains, in which are enlargements for collection of spray and moisture, which runs back into the

cell. Current densities of 2 to 3 amperes per square decimeter are possible with a working voltage between 2.45 and 3, using caustic soda solution of 21° Bé. The cell shown in Fig. 191 is intended to take 400 amperes, and to require 1 kilowatt of power.

6009. Another Garuti generator consists of 45 separate compartments made of 16-gauge sheet iron welded together to form a single unit.² The sides of the compartments are used as diaphragms and are usually perforated (Fig. 192) to allow circulation of the electrolyte but not the gas. The perforations extend lengthwise along the lower edge of each compartment wall 3 in. from the bottom, forming a perforate strip 2½ in. wide. An electrode is placed in each compartment and the electrodes are alternately positive and negative. All like electrodes are connected together. Each compartment is ¾ in. in width and 30 in. long.

6010. The electrodes are insulated from the compartments and are prevented from coming in contact with the walls by means of small porcelain insulators. The gas from all of the hydrogen-producing compartments is collected in a gas bell welded to one side of the cell proper and is led through a water seal and to a header pipe and then to a gasometer. The oxygen gas is handled in a like manner. The cells as well as the container tanks and pipe lines are insulated from the ground. The pipe from the cell to the header pipe is insulated from the latter by means of a sleeve of rubber and glass.³

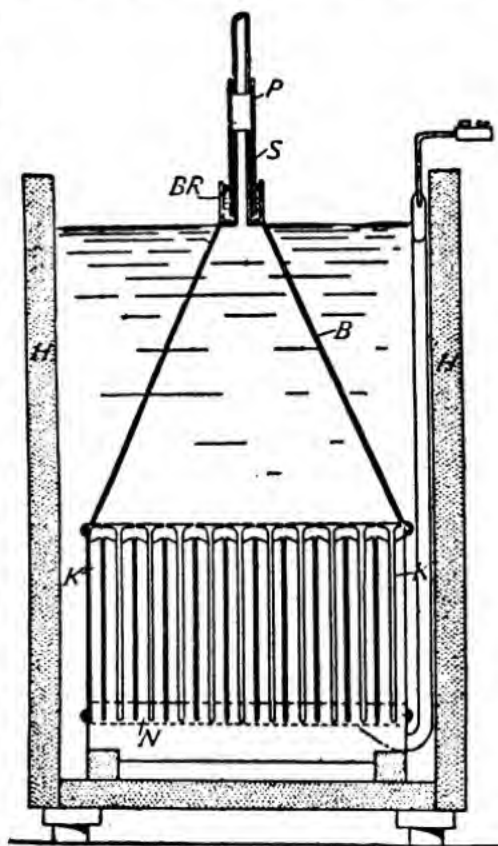


FIG. 190.

² In 1892 Garuti took out a patent (Brit. Pat. 15,588, Apr. 25, 1892) describing an apparatus consisting of a container having an inverted leaden case with partitions of sheet lead soldered together so as to form a case divided into parallel cells open only to the water at the bottom. The partitions of the cells separate the anodes and cathodes which are placed alternately and are insulated in the cells by means of combs made of suitable material. In 1896 Garuti and Pompili (Brit. Pat. 23,663, Oct. 24, 1896) described an improvement on the former patent, involving the perforation of the diaphragms in their lower part by small holes as near as possible to each other. See also U. S. Pat. to Garuti 534,259, Feb. 19, 1895, and Garuti and Pompili 629,070, July 18, 1899.

³ When the Garuti cell is first installed the efficiency will often be as high as 6 cu. ft. or so of hydrogen per kw.-hour, but the depreciation is said to be perhaps more rapid than in some other types of generators and in time the hydrogen output may drop to about 5 cu. ft. Thus under the normal operating amperage of 350 to 400, from 2½ to 3 volts per cell will be required. The rather rapid depreciation of the generator is said to have held back its use to some extent. Owing to the lightness of the materials employed and also possibly because of insufficient

6011. Siemens Bros. & Co. and Obach devised the apparatus shown in Fig. 199, the principle being similar to that of the Garuti. The cast-iron vessel *a* is

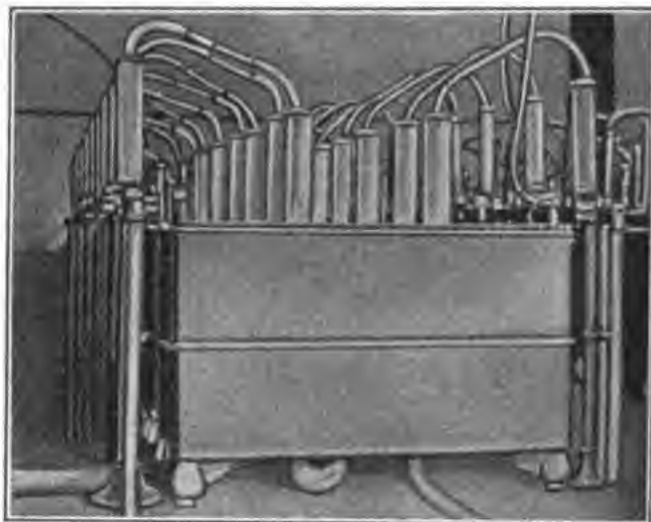


FIG. 191.

surrounded by heat-retaining material, in order that the temperature of the cell may be automatically raised and thus its running resistance lowered. A cylin-

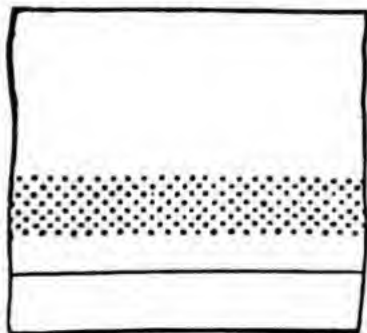


FIG. 192.



FIG. 193.

PERFORATED COMPARTMENT WALLS OF THE GARUTI GENERATOR.

drical iron anode *f* is separated from the encircling cathode *g* by a cylinder of wire netting *c*, held in place by the porcelain block *k*. The electrolyte is dilute

electrode surface, the anode is liable to be attacked and eventually worn away. The minute particles of iron or iron compounds formed are said to have a tendency to be deposited on the cathode. The insulators, employed to prevent the contact of electrode with the compartment wall, form a convenient place of deposit for the iron particles with possible danger of causing a short circuit between the electrode and the compartment walls. If one compartment is short circuited the entire cell becomes "shorted" and this short circuit will cause the generation of mixed gas. The entire cell should be dismantled about once a year and cleaned with either a stream of water or by means of a sand blast.

The American Oxhydric Company, Milwaukee, Wis., have used generators of the Garuti type.

caustic soda; the gases escape above from the spaces *n* and *m*. The whole apparatus is set on insulating porcelain feet. The normal type of apparatus is built to take 750 amperes at 3 volts drop of potential, and furnishing 11 cu. m. of oxygen and 22 cu. m. of hydrogen per twenty-four hours, using up 162 kilowatt-hours.⁴

6012. Fiersot describes⁵ an apparatus of Siemens and Halske for the electrolysis of water in which a 10 per cent solution of potassium carbonate is used as electrolyte. One hundred and thirty-four grams of water are decomposed per kilowatt-hour. By heating the electrolyte the output may be increased by 8 per cent. The electrolytic oxygen thus produced is on the average 97 per cent pure, while the hydrogen contains 1 per cent of oxygen.

6013. Another form of metallic diaphragm cell has been devised by Fischer, Luening and Collins.⁶ The generator consists of a tank containing an electrolyte in which an indifferent number of independent, preferably oblong, metallic cases are submerged. An illustration of the case is shown in Fig. 201. The case is open at the bottom and is divided into a pair of cells by a metallic diaphragm. Electrical connections to the anode and cathode and exit pipes situated on the upper side of the case are provided for the removal of the gases.

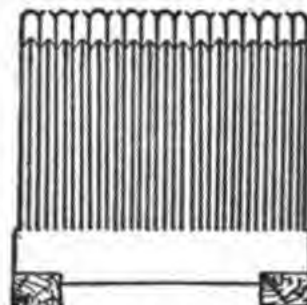


FIG. 194. — COMPARTMENTS OF THE GARUTI GENERATOR.

6014. The electrolytic cell of Tommasini as shown in Fig. 202 contains vertical anodes 6 and cathodes in the form of inverted U-shaped receptacles 5. The outside of these receptacles 5 is covered with an insulating apron 7 which extends to a point above the liquid line, and to a point below the lower edge of the cathode 5 proper, so that an overhanging apron 8 is provided. The gases evolved at the plates 6 and accumulated in the top of the inverted receptacles 5 are conducted off separately, the hydrogen passing through the pipe 12 into the safety device 14. The height of water in the safety device 14 than in the receptacles 5, so that when the pressure of the hydrogen gas becomes so great as to tend to press the fluid out of the chambers 5 (which would result in the mixing of the hydrogen with oxygen) the pressure of the hydrogen gas will first press the water out of the receptacle 19 and pass out of slots 20, so as to relieve the pressure in the receptacles 5. The aprons 8 at the bottom of the compartments 5 also prevent mixing of the two gases.⁷

6015. Buffa,⁸ writing of metal partition electrolytic cells, says that, in practice, iron electrodes in a 11 per cent solution of caustic soda have been found to be most convenient and economical. The electrolyte is covered with a film of mineral oil, in order to prevent absorption of carbon dioxide from the air. It has been observed that the same protective action is afforded by a film of water vapor, which obtains when the temperature of the electrode is fairly high; when, however, the temperature drops to 10° C. or under, absorption of carbon dioxide takes place rapidly.

6016. The multiple cell of Schmidt⁹ looks somewhat like a filter press, Fig. 203, and consists essentially of bipolar iron electrodes connected in series. Each

⁴ *Jour. Franklin Inst.*, 1905, 392.

⁵ *Electrochemical Ind.*, 1904, 28.

⁶ U. S. Pat. 1,004,249, Sept. 26, 1911.

⁷ U. S. Pat. 1,035,000, Aug. 6, 1912.

⁸ *Electrician*, 1900, 46.

⁹ Ger. Pat. 111,131, June 13, 1899.

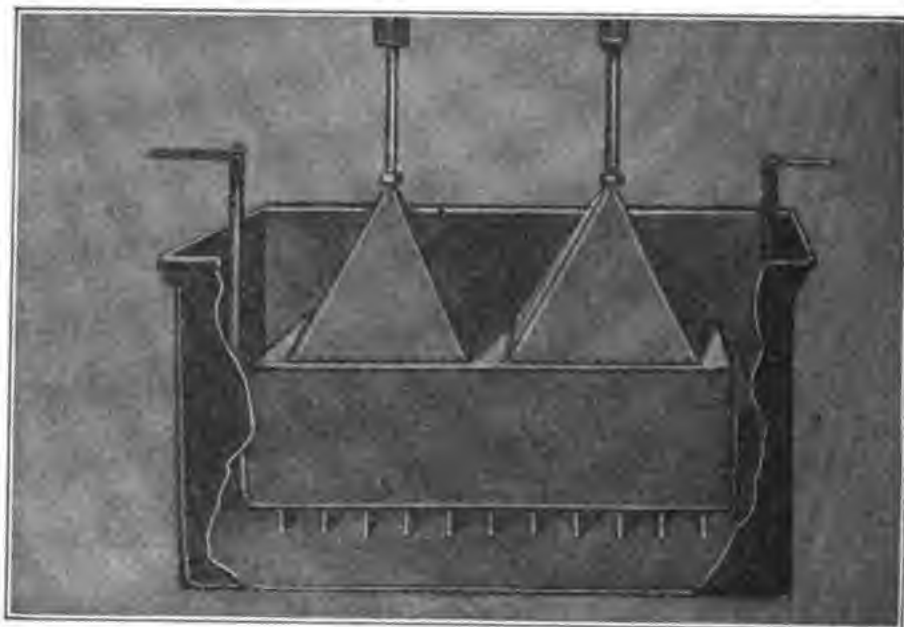


FIG. 195.—GARUTI GENERATOR.

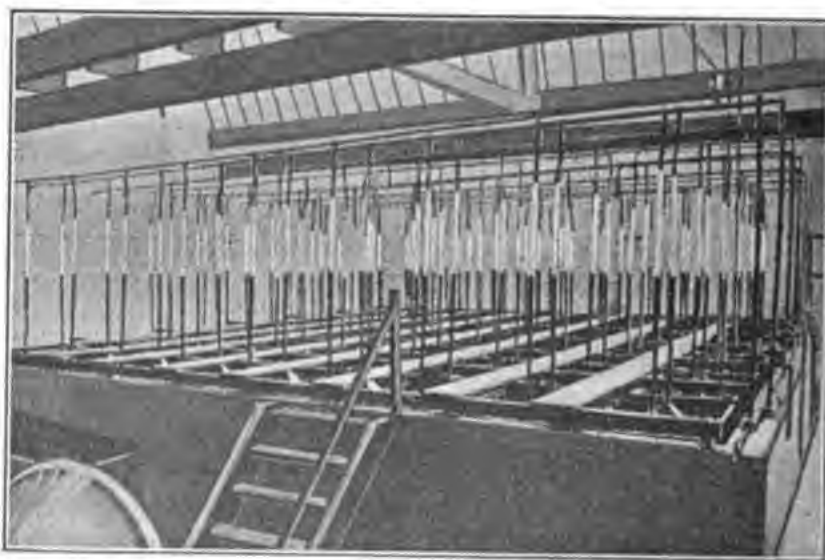


FIG. 196.—BATTERY OF GARUTI GENBRATORS.

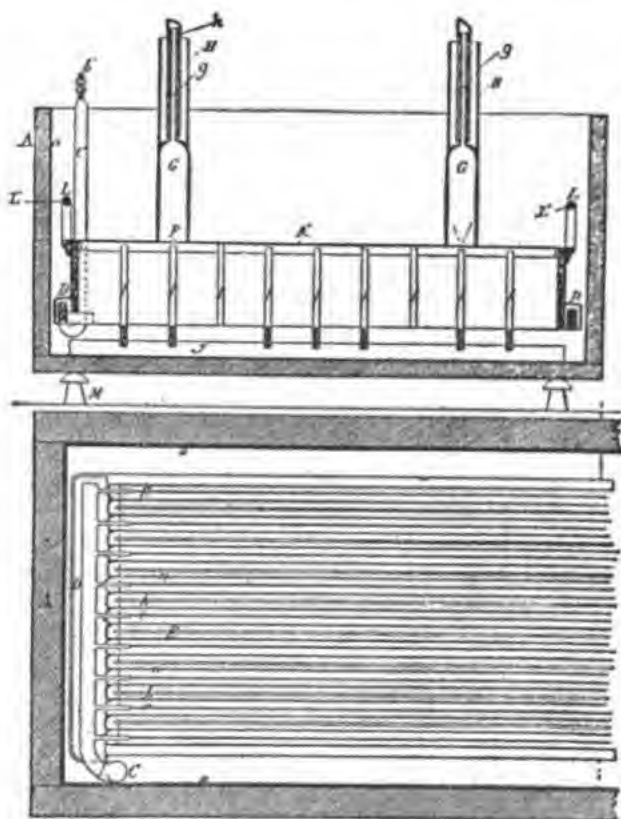


FIG. 197.—ONE FORM OF THE GARUTI GENERATOR.

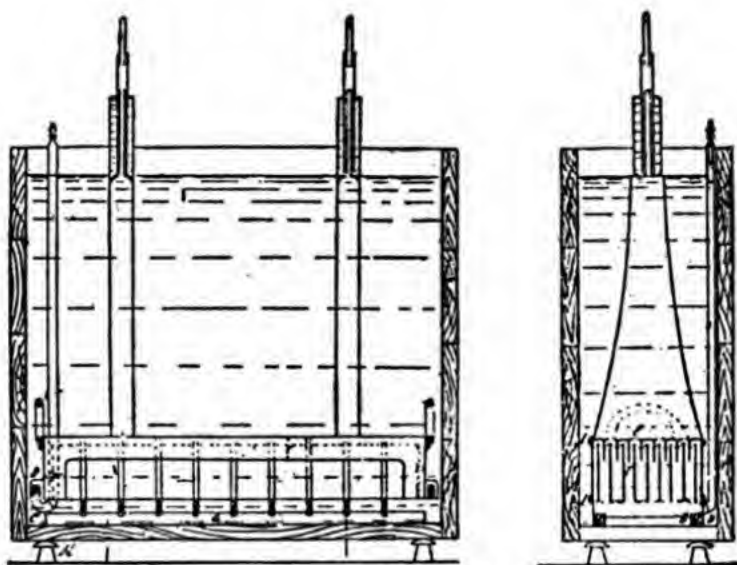


FIG. 198.—A MODIFIED FORM OF THE GARUTI GENERATOR.

frame in the press contains an iron electrode, which acts as a double-pole (bipolar) electrode, sheets of asbestos cloth held between the frames acting as partitions, reinforced with rubber on the edges for making tight joints. The electrolyte is a 10 per cent solution of potassium carbonate, filled into the apparatus through the standpipe on the right, which communicates with all the compartments through holes in the frames similar to the usual filter-press construction. The gases evolved escape by similar passages into the cylinders on the left end, where

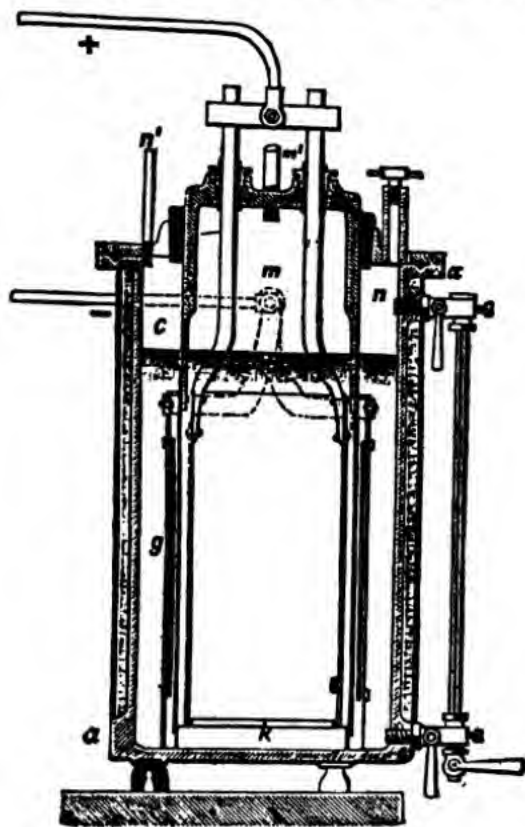
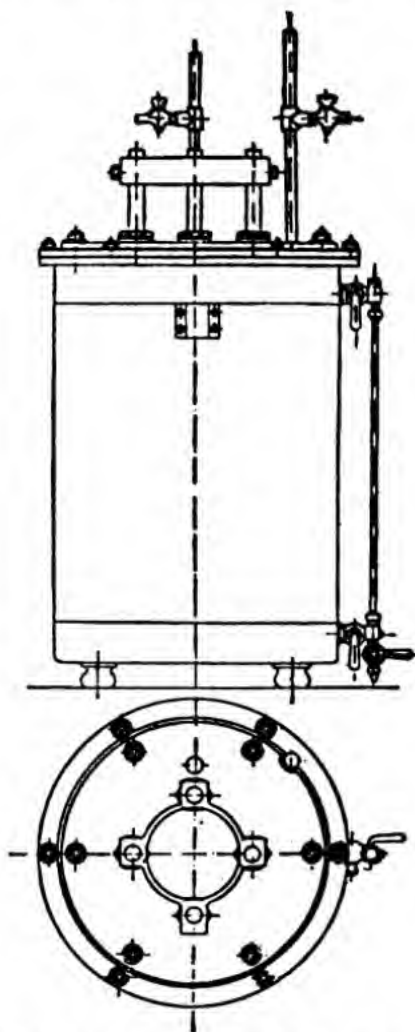


FIG. 199.

FIG. 200.—PLAN AND ELEVATION OF
SIEMENS BROS. AND OBACH GENERATOR.

they separate from the electrolyte and pass upwards, while the electrolyte, dragged by the gas bubbles, flows downwards back into the apparatus, thus maintaining an efficient circulation. With forty plates about 2.5 volts are absorbed in each cell, using a current density of about 2 amperes per square decimeter.

6017. The apparatus is shown in detail in Fig. 204. A 110-volt direct-current lighting circuit may be employed for the operation of a series type apparatus composed of the requisite number of cells. The press has to be taken

apart and cleaned every six weeks and the asbestos diaphragms have to be renewed from time to time.

6018. An electrolyzer for the production of pure hydrogen and oxygen which is suggestive of the Schmidt type has been designed by Eycken, Leroy and Moritz.¹⁰ The electrode plates

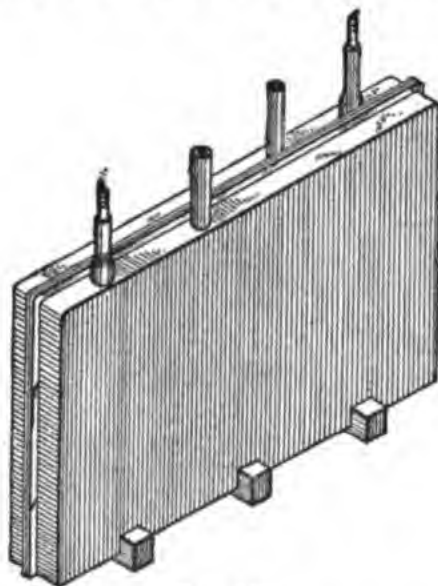


FIG. 201.

are built up with separating diaphragms of asbestos, in the form of a filter-press. Openings in the top of each plate form two channels for the escape of the gases. The gases are kept at a pressure above that of the atmosphere, rendering the danger of accidental mixing remote. The electrodes and diaphragms are kept clean by making the first electrode hollow, and in

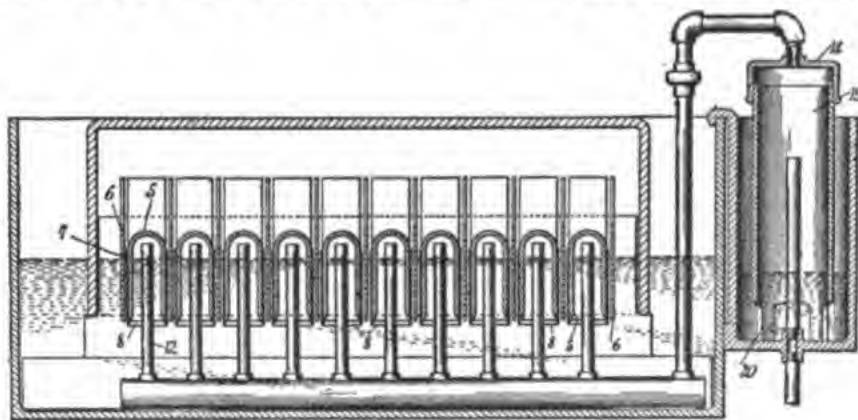


FIG. 202.

the form of a large reservoir, in which the sediment accumulates and from which it may be removed from time to time. This reservoir is divided into two parts, into which the gases pass, through the electrolyte, the pressure being maintained constant, and the delivery of the gases regulated by two floats and balanced valves.

¹⁰ French Pat. 397,319, Dec. 9, 1908.

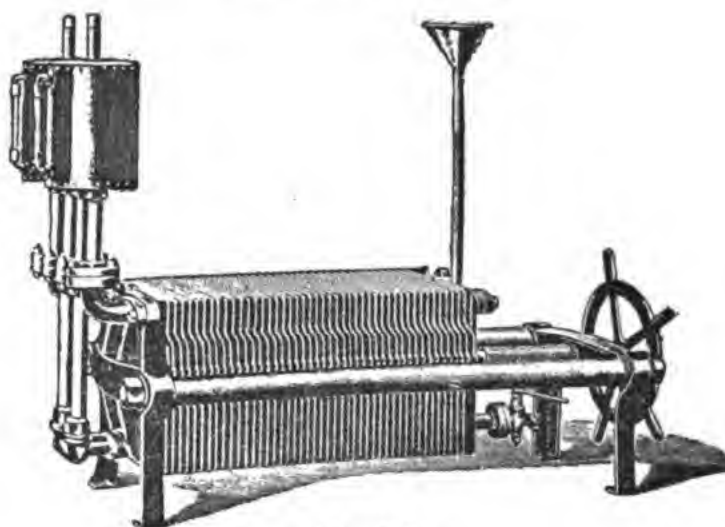


FIG. 203.

6019. Siegfried Barth of Düsseldorf has built "oxhydrogenerators" constructed in accordance with the foregoing system. The parts of the generator are very heavy so that durability is insured. The electrode plates are insulated by extra heavy, almost indestructible, diaphragms. A very powerful circulation of the electrolyte over the surface of the electrode is obtained, resulting in an efficient removal of the gas particles which otherwise would cling to the electrodes for a considerably longer period. Great pains have been taken to guard against mixing of the gases so as to procure pure products. Caustic soda or potash in distilled water is used as the electrolyte. When used uninterruptedly, the cell becomes warm and its output is improved, and for intermittent operation a steam-heating arrangement is attached to the generator so that it may be heated quickly and brought to full capacity without loss of time. The ordinary type of this generator is made to deliver both hydrogen and oxygen under a pressure of about 50 to 80 cu. m. water column, but special forms are furnished which operate under a pressure of about 4 kilos (8 to 9 pounds). A generator having an output of 6.6 cu. m. of hydrogen and 3.3 cu. m. of oxygen per hour, requiring 160 amperes at 250 volts is 4.4 m. long, 0.72 m. wide, and 2.05 m. in height, and weighs 6600 kilos. (Fig. 205.)

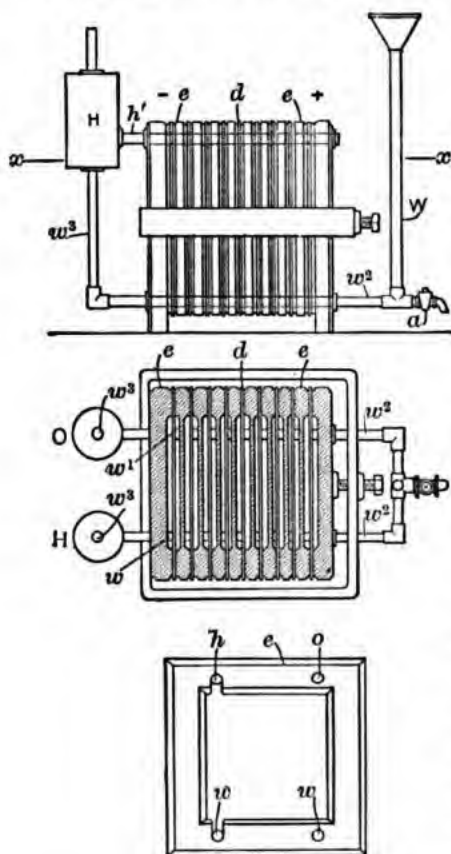


FIG. 204.

6020. Another apparatus of the filter-press type ¹¹ is designed especially to produce the gases at relatively high pressure without the purity of the product being affected. Fig. 206 shows a form of electrode plate and Fig. 207 a view of one end of the generator, showing a collecting tower with regulator float and a series of plate electrodes. ¹²

¹¹ Moritz, U. S. Pat. 981,102, Jan. 10, 1911.

¹² In the generator of L'Oxyhydrique française (French Pat. 459,967, Sept. 21, 1912, and addition, June 25, 1913), the diaphragm of each

6021. Shriver ¹³ devised an apparatus composed of several flat plates, forming the electrodes, bound face to face to form a cell of the filter-press type, each of the plates being recessed centrally to form a cell between the faces. A diaphragm is arranged between each pair of plates to separate the gases formed on the faces of adjacent plates, the gases being led from the recessed portions to closed gas chambers above, through ducts in walls separating the chambers and recesses. The gases are conveyed from the gas chambers to horizontal ducts extending through non-recessed parts of the plates from face to face, so that the recessed portions may be completely filled with liquid to a level normally higher than the horizontal ducts, without fear of the electrolyte entering the gas ducts.¹⁴ See Fig. 208.

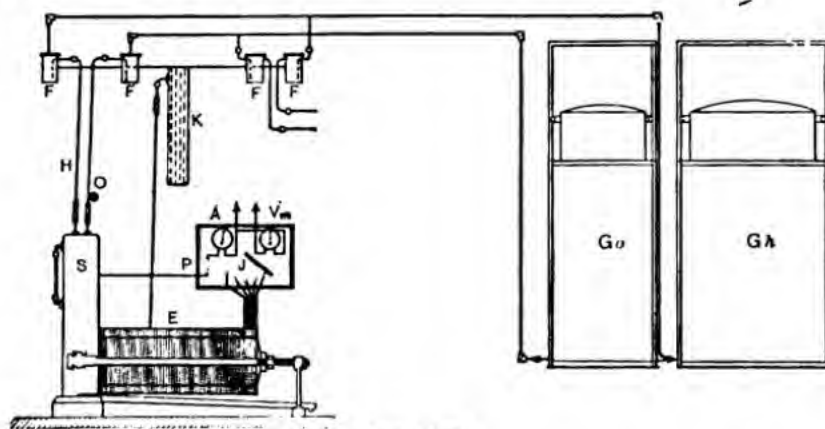


FIG. 205.

6022. The International Oxygen Company has developed an oxygen and hydrogen generator of the filter-press type under the name of the I.O.C. bipolar generator.¹⁵ See Figs. 209, 210 and 211. The unit type of generator produces 3.2 cu. ft. of oxygen and 6.4 cu. ft. of hydrogen per clock hour and 4 cu. ft. of oxygen and 8 cu. ft. of hydrogen per kilowatt hour.

6023. The I.O.C. Bipolar Generator consists of a series of metallic plates (electrodes) clamped together in a heavy frame, electrically insulated from one another and separated by diaphragms of porous fabric. Each pair of these electrodes forms a closed cell, divided by the diaphragm. These cells are filled with an alkaline electrolyte (caustic potash or soda). An electric current admitted at one end plate passes on through the plates and the solution to the other end plate. In its passage, it decomposes the water in the solution into the two gases—oxygen and hydrogen which are released on opposite sides of each plate and emerge upward into the gas offtakes.

element is composed of asbestos fabric, which is nipped between two wooden frames. The latter are bored so as to provide conduits for the evolved gases and the electrolyte. The electrodes are composed of light sheet iron, grooved or corrugated, so as to possess as much active surface as possible. The electrodes may be nicked on their anode sides. The apparatus comprises a series of such elements. See also U. S. Pat. *Reissue* 13,643, Nov. 11, 1913.

¹³ U. S. Pat. 1,181,549; *J.S.C.I.*, 1916, 1023.

¹⁴ See also U. S. Pat. 1,239,530, Sept. 11, 1917; *J.S.C.I.*, 1917, 295.

¹⁵ Levin, U. S. Pat. 1,094,728; French Pat. 467,945, Jan. 31, 1914; Brit. Pat. 3,654, Feb. 12, 1914; *Met. Chem. Eng.*, 1916, 108; U. S. Pat. 1,199,472. Hepburn has designed a bipolar generator (U. S. Pat. 1,213,871; Brit. Pat. 12,730, 1915).

6024. The mingling of the oxygen and hydrogen in each cell or compartment is prevented by the diaphragm and, as the gases are released and withdrawn, the solution is automatically replenished from a supply tank. The operation is continuous so long as current and electrolyte are supplied. In the smaller type of generator, the electrodes are carried on two steel rods supported on two heavy end pieces or pedestals of cast iron. In the larger generator, the side rods are replaced by steel bars. The construction is one of extreme rigidity, absolutely proof against any distortion and consequent disarrangement of electrodes, with resultant leakage. The electrodes are clamped together by a heavy screw working in the rear support. A ball thrust bearing is interposed between the end of the clamping screw and the rear end plate, contributing to the tightness of the generator by doing away with the tendency of the electrodes to "ride up" from the side bars under screw pressure. The electrodes are of a special design,¹⁶ the anode side being heavily nicked, while the cathode side of commercially pure iron. The surfaces of the electrodes carry vertical corrugations which are interrupted by a large number of depressions to facilitate the flow of electrolyte into the cell and the release of the gases from it. At top and bottom of each electrode are two openings communicating by a cored channel with opposite sides of the plate. Those at the bottom are for the water intake and those at the top are for the gas offtake. Each half of each cell (separated by the diaphragm) has its own independent water intake and gas outlet, so that there can be no possibility of the two gases mingling through these channels. Any gas leakage which may occur between the electrodes escapes to the open air and not into the adjacent cell or into the gas offtakes. The diaphragms are of especially prepared asbestos fabric. All around the edge of this fabric is molded a packing rim of pure rubber which rests in a recessed groove on the face of the electrode.

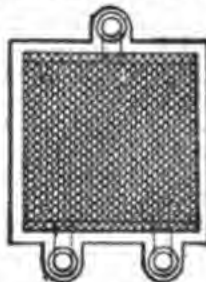


FIG. 206.

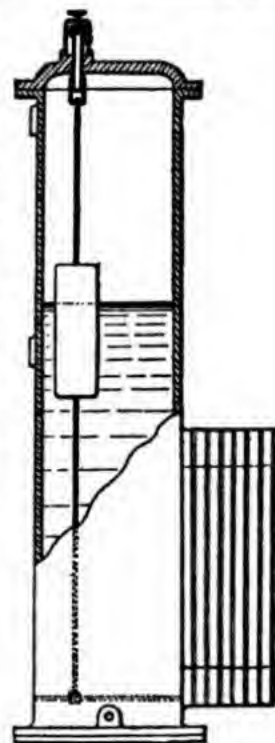


FIG. 207.

6025. In a generator of this kind, an essential of power economy is that all the current supplied the machine shall pass through the electrolyte and none of it be by-passed through the metal of the machine or through the water inlets and gas outlets. The electrodes are insulated from the side bars of the frames by porcelain insulators. The electrodes are insulated from one another by the pure rubber packing rim surrounding the diaphragm, and by nipples of pure rubber inserted in the water intake and gas offtake shoulders of the electrodes. These nipples, when the apparatus is closed, meet one another and not only insulate the electrode shoulders but also provide an insulating tube in the interior of the water intakes and gas offtakes. The gases rising from the electrodes and entering the gas offtakes, carry with them a small percentage of the electrolyte which, if allowed to enter the external piping system, would "ground" the apparatus and permit the escape of current. To guard against this contingency, there is provided in the gas offtake system insulating pipe sections, each consisting of two sections of heavy glass tube clamped between iron flanges and so devised as to intercept and drain off through an insulating connection the moisture entrained in the gases. The gases go through these insulators substantially dry and free from electrolyte. The nickel anode and iron cathode have been found to materially facilitate the electrolysis, and to lower the over-voltage. Incidentally, these bi-metallic electrodes prevent the formation of rust and oxides which would shorten the life of the apparatus. The design of the generator is such as to retain within the apparatus most of the heat produced as a result of the resistance to the flow of electricity. This keeps the electrolyte and the electrodes at a comparatively high temperature, which adds to the efficiency of the electrolytic process. On the front of the generator are two tanks with glass water-level indicators, which carry the solution. Pipes descend from these tanks to a water-feed manifold which branches into two pipes connecting independently to the two water intakes to the cells and also into two risers leading to two independent gas

¹⁶ U. S. Pat. 1,153,168 to Levin.

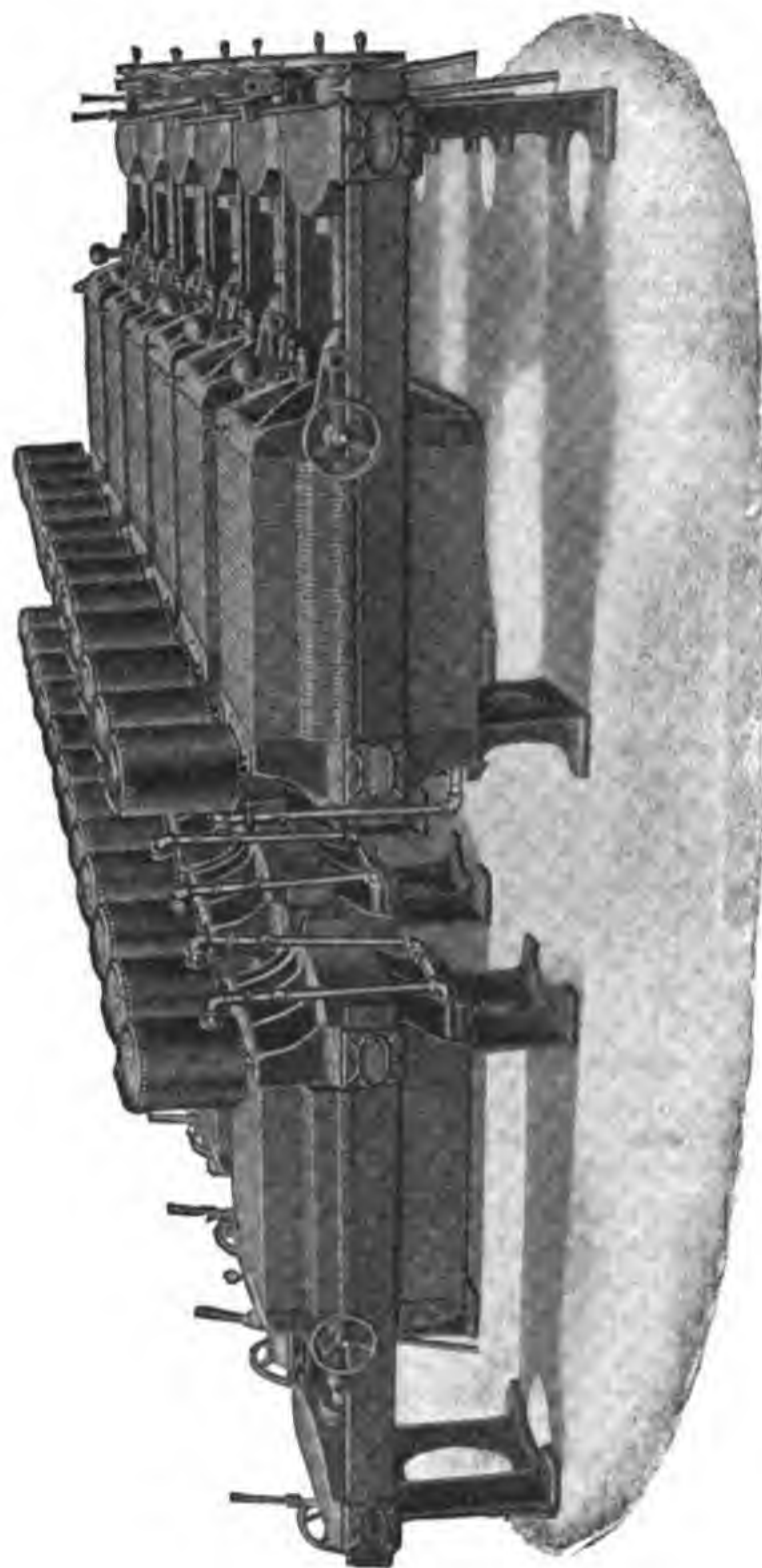


FIG. 208.—SHRIVER OXY-HYDROGEN GENERATOR.

domes above. Into these domes, the oxygen and hydrogen are separately discharged as generated, the gas offtakes opening through an inverted "U" below the fluid level. The proper fluid level is automatically maintained throughout the system. The two independent water intakes to either side of each electrode prevent mingling of oxygen and hydrogen through the water supply. The two gas off-takes discharge into the two independent gas domes already referred to, the gas emerging below the fluid surface through an inverted "U." The pressure on both gases, clear back to the individual cells, is the same—this being controlled by the hydrostatic head in the domes through which the gases pass. The gases escaping from the gas offtakes rise through the fluid in the gas domes and pass out through discharge pipes at the top of the domes—thence downward to purgers on either side. These purgers are closed boxes of cast iron filled with water to a certain level. The gases escape below the surface of the water, and pass upward through it into the supply lines to the gas holders. The function of these purgers is to catch any entrained electrolyte in the gas, to cool the gas, and to act as a water-check valve protecting the pressure system of the generator from any undue pressure

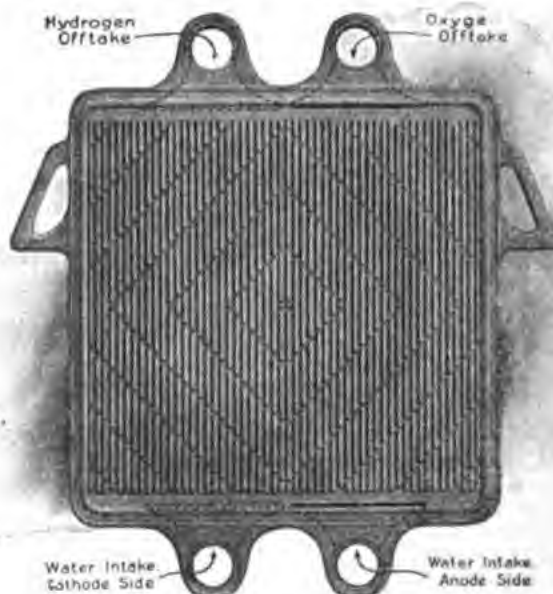


FIG. 209.

of the gasholders. A signal whistle is provided which gives notice when the level of the solution in the generator falls below the prescribed level. Glass sight-feed indicators on the solution tank and gas domes show the fluid level and reveal the generation of the gases. Gauge glasses connecting with the electrodes at intervals along the generators show the fluid levels in the body of the apparatus.

6026. Figures 212 and 213 show a single section or unit and Fig. 213a indicates the method of assembling the sections of a compact form of hydrogen generator developed by the International Oxygen Company. Although of the single unit type, the cell is but $3\frac{1}{2}$ in. thick and in consequence 100 cells can be stacked in a lengthwise space of less than 30 ft. The cells are approximately 3 ft. 6 in. wide and as installed are not in excess of 6 ft. high. They occupy less space than the filter-press type. These unit cells when operating at their normal current of 600 amperes will produce 4.8 cu. ft. of oxygen and 9.6 cu. ft. of hydrogen per clock hour. They require 2.22 volts per cell, which establishes a kw.h. efficiency of 3.65 cu. ft. of oxygen. When operated at a current less than 600 amperes the electrical efficiency is considerably increased but the capacity is decreased and when operated in excess of 600 amperes there is an

increased capacity but a slight falling off in electrical efficiency; 600 amperes has, therefore, been adopted as a compromise between initial cost of installation and operating cost.

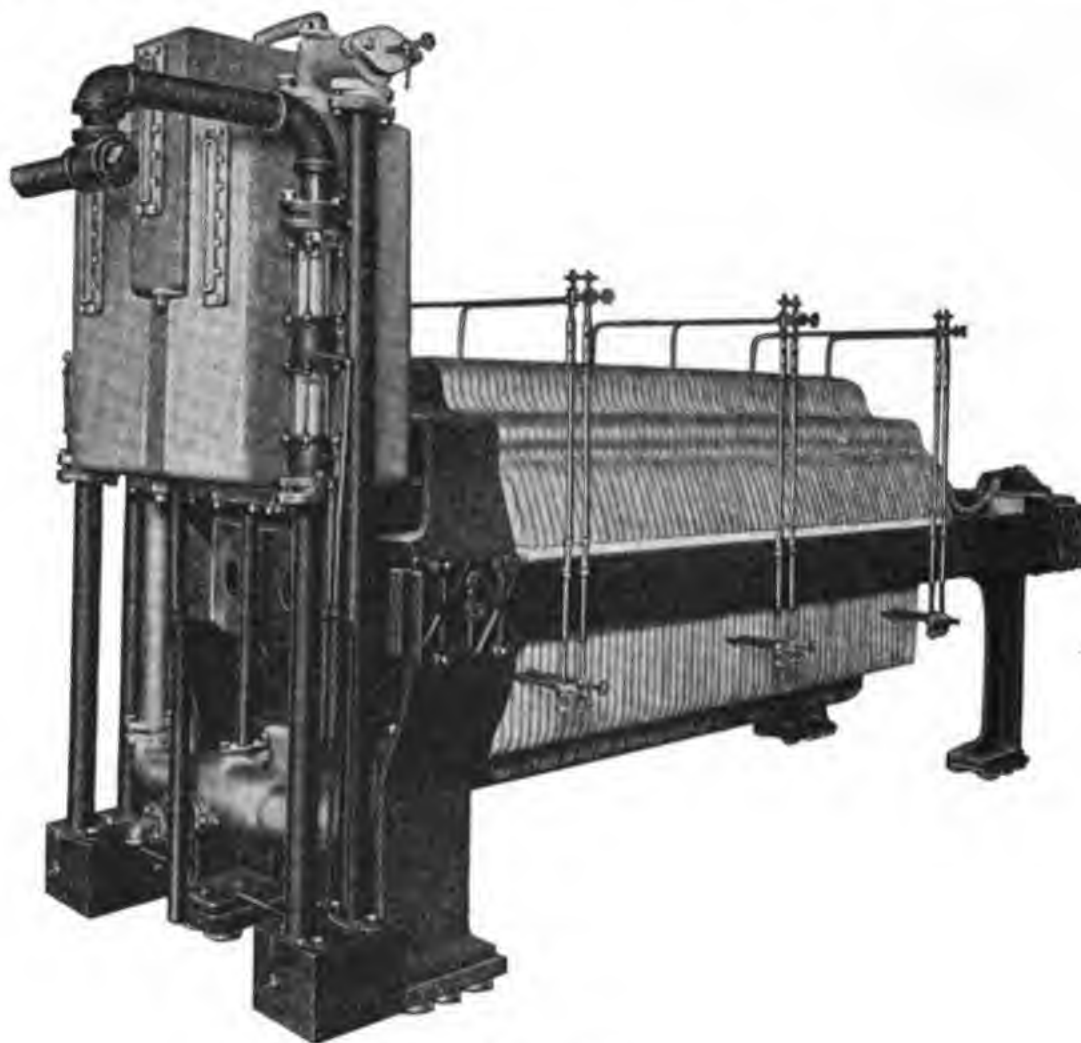


FIG. 210.

6027. As indicating the flexibility of this equipment there is tabulated below, the approximate performance at currents up to as high as 1000 amperes.

Current	Volts per Cell	Cu. ft. Oxygen per Hour	Cu. ft. Hydrogen per Hour	Cu. ft. Oxygen per KWH	Cu. ft. Hydrogen per KWH
300	1.94	2.4	4.8	4.17	8.34
400	2.04	3.2	6.4	3.97	7.94
500	2.13	4.0	8.0	3.80	7.60
600	2.22	4.8	9.6	3.65	7.30
800	2.38	6.4	12.8	3.40	6.80
1000	2.54	8.0	16.0	3.16	6.32

6028. An electrolytic apparatus, of the filter-press type, designed by Dohmen ¹⁷ is composed of a series of cells, each comprising a thin quadrilateral wrought-iron frame having a single central opening, and with two passages through the top of the frame. A detachable sheet metal electrode is secured in the opening of the frame, and the top of the latter is also provided with two gas-separating chambers one at each end. The chambers extend laterally in a downward direction to the active faces of the electrodes for conducting the gases from opposite sides to the two passages.

6029. Schoop, in 1900, devised an apparatus with non-conducting and non-porous partitions, which once had considerable commercial use. Figure 214

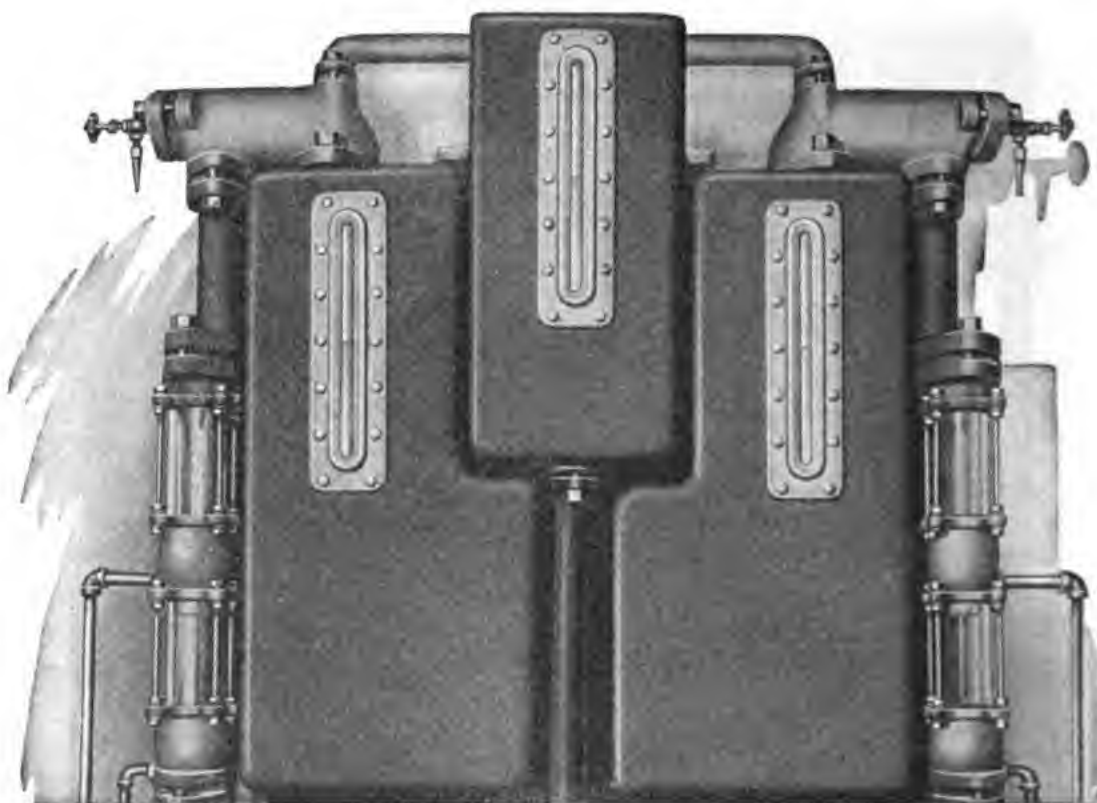


FIG. 211.

shows the section of the apparatus, where *aa* are the tubular electrodes of sheet hard lead, enclosed by glass or clay suspended tubes *c*, which are perforated at their lower end; the electrode surface is further increased by fine hard lead or iron wires hung inside the tubular electrodes, the latter being perforated above the level of the electrolyte in order to let the internally generated gas escape. Each cylinder contains two anodes and two cathodes. When alkaline electrolytes are used and iron electrodes, the working voltage is 2.25; when sulphuric acid of density 1.235 is used, with hard-lead electrodes, the working voltage is

¹⁷ U. S. Pat. 1,211,687, Jan. 9, 1917, *J.S.C.I.*, **1917**, 295.

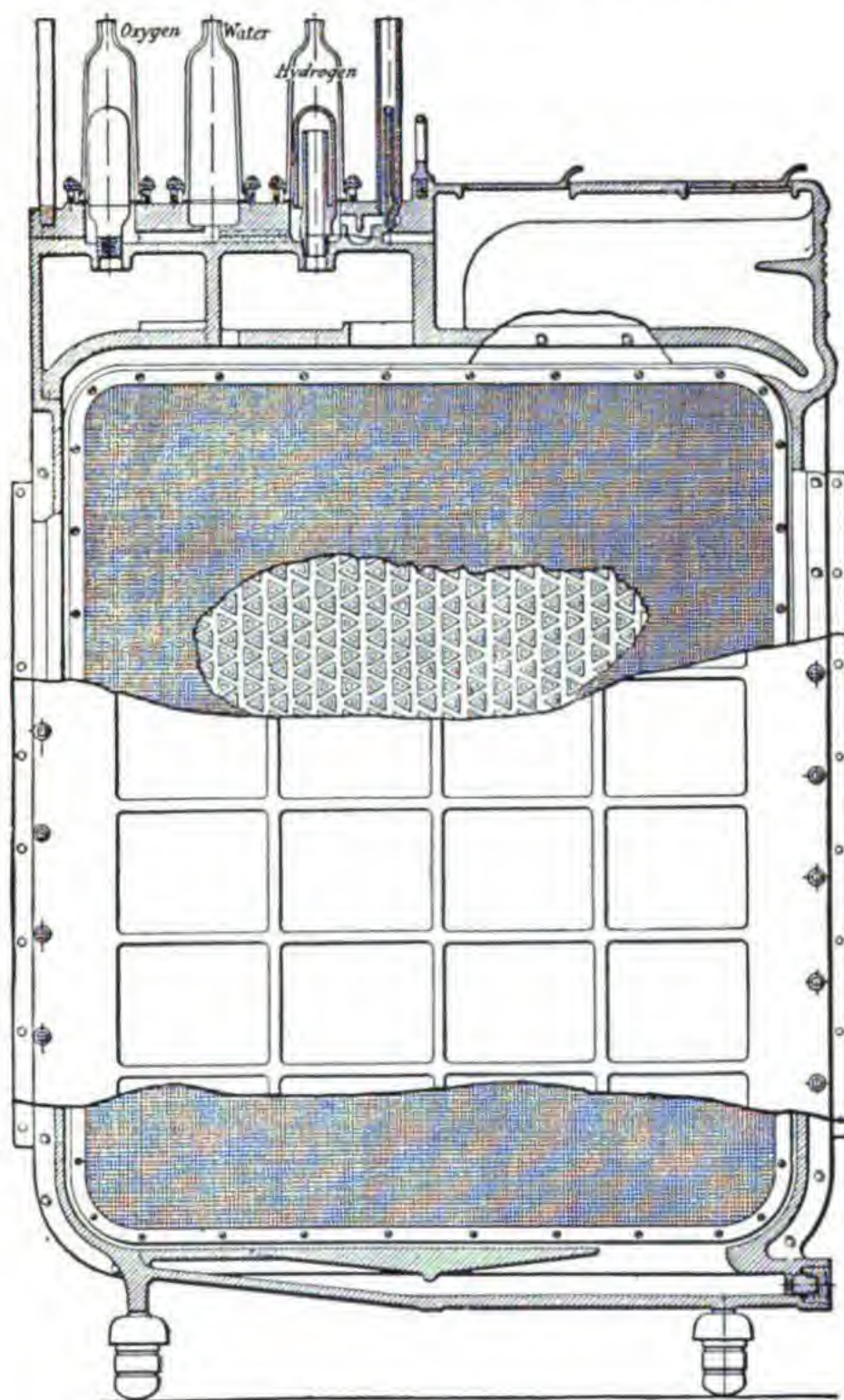


FIG. 212.

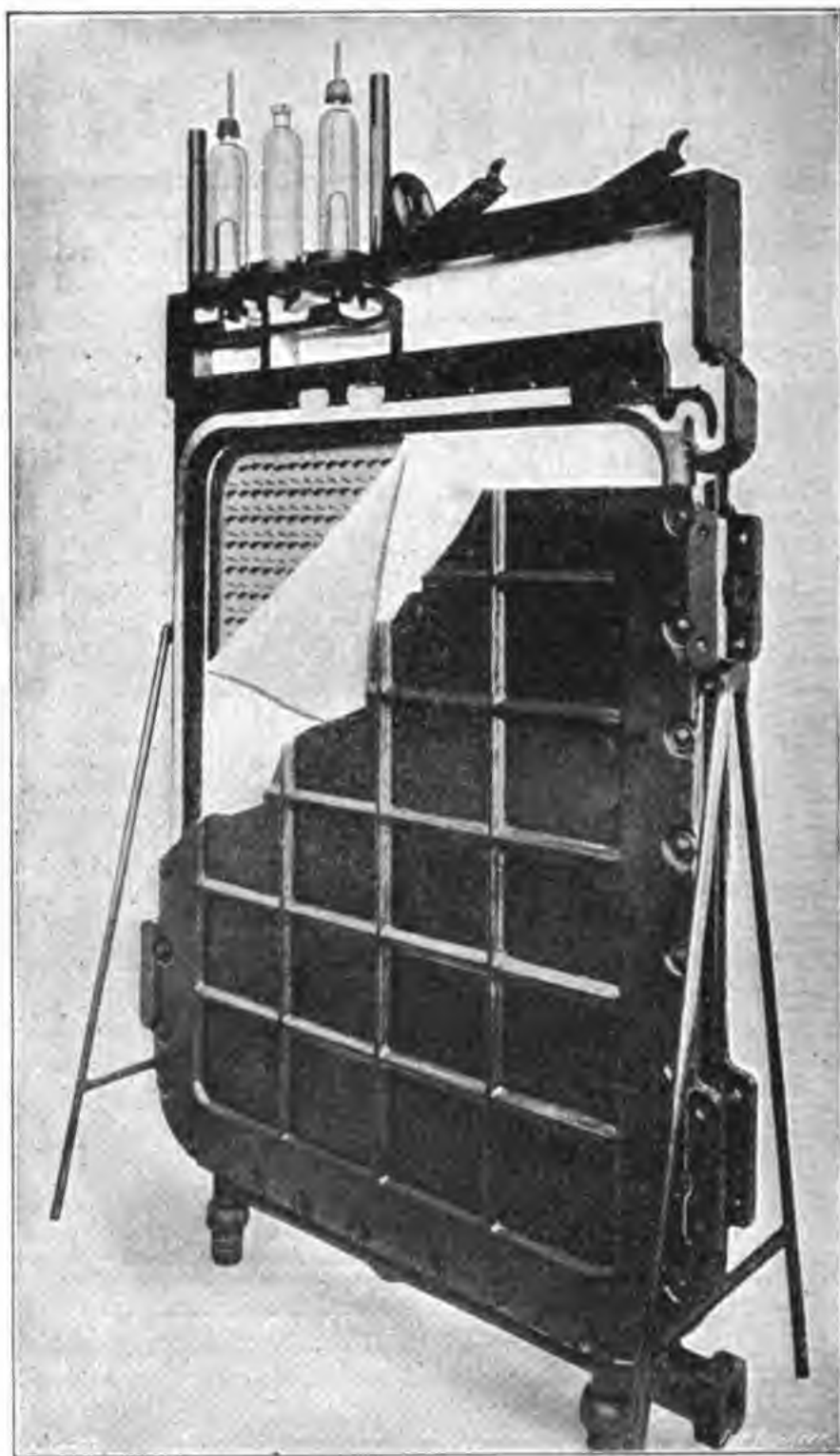


FIG. 213.

3.6 to 3.9. Fig. 215 shows a single electrode and Fig. 216 an installation of the Schoop system.¹⁸

6030. Details of construction of an electrolytic apparatus for the production of hydrogen and oxygen are given by Van Scoyoc¹⁹ in which the operation is rendered continuous by the use of automatic float-valves. The level of the acidulated water in the electrolyzer is main-

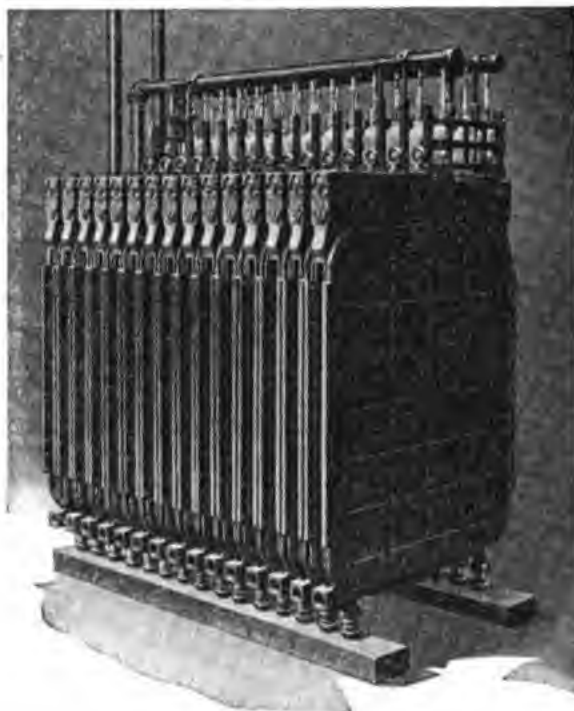


FIG. 213a.

tained constant by means of a float-valve in the supply pipe. The two electrodes are placed in two compartments which are open at the bottom. Each compartment is divided into a lower and an upper chamber, connection between the two being made by automatic float-valves. When the pressure of the gases generated in the lower chambers becomes great enough to lower the level of the water, the valve is opened and the gases pass into the other chamber and then into gas bags.

¹⁸ Schoop (*Zeitschr. Elektrotechn. Wien*, 1900, 18, 441) discusses the difficulties met with in the construction of a suitable apparatus for the technical electrolytic manufacture of hydrogen and oxygen, and gives a description of patents dealing with this subject. In the Schoop apparatus it is claimed that 1.5 cu. m. of hydrogen and oxygen are produced per 11 horse-power hours. Richards (*Jour. Franklin Inst.*, 1905, 390) notes that the output is given as 68 liters of oxygen and 136 liters of hydrogen per electrical horse-power hour. A description of the Schoop system is given in the *Centralblatt f. Accum.*, Feb. 15, 1903. It is stated that the length of the tubes is chosen according to the pressure under which the gases are wanted. The following results were obtained with the Schoop apparatus during one year: One electric horse-power hour gives 97.5 liters of hydrogen and 48.75 oxygen (probably under atmospheric pressure); i.e., for 1 cu. m. of mixed gas 6.8 horse-power hours are required; with warm acid (sulphuric acid of 1.23 specific gravity being always used) this value is reduced to 6.2 horse-power hours; if the price of one horse-power is 1 cent, the cost of the production of 1 cu. m. of mixed gases is 4.2 to 4.8 cents. The purity of the oxygen is 99 per cent, that of the hydrogen 97.5 to 98 per cent.

¹⁹ U. S. Pat. 813,844, Feb. 27, 1906.

6031. Aigner charges an alkaline electrolyte into an iron vessel *G*, Fig. 217, in which an iron drum *T* rotates, the outer surface of the latter being amalgamated. The upper part of

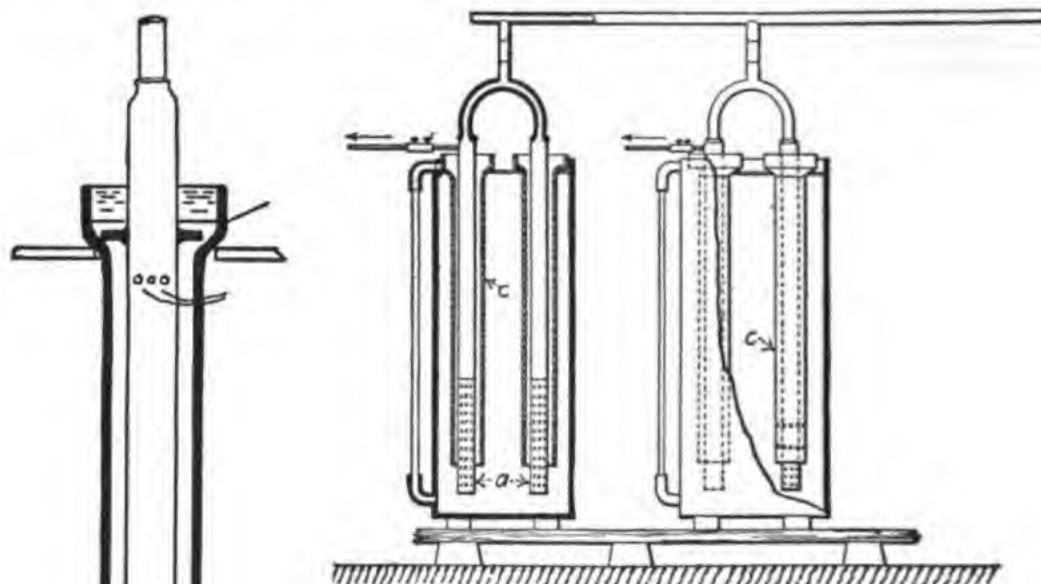


FIG. 214.

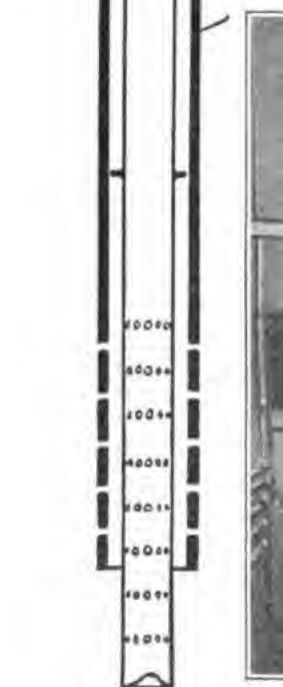


FIG. 215.

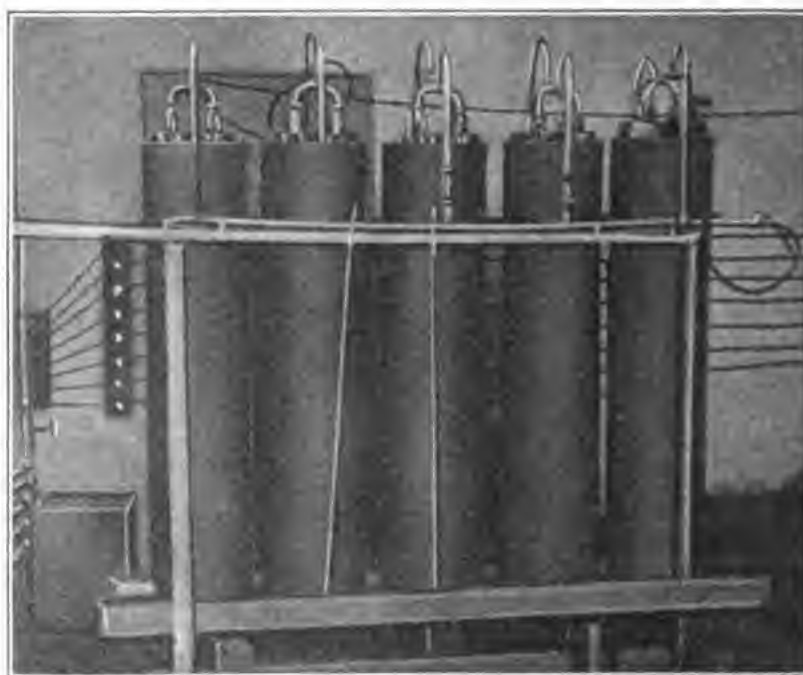


FIG. 216.

G is divided into two compartments *R* and *R*₁ by the partition *S*, which extends downwards nearly to the drum *T*. The oxygen and hydrogen are led off through separate outlets in the cover *D*. The electrolyte is introduced and withdrawn through the opening *L*. At the anode

A hydroxyl ions are depolarized, with formation of water and gaseous oxygen, the latter escaping into the compartment *R*, while an equivalent quantity of sodium ions is depolarized and combines chemically with amalgam on the surface of the drum adjacent to the anode. When this portion of the drum comes below the cathode *K* hydroxyl ions are depolarized with formation of sodium hydroxide, the sodium being redissolved from amalgam, while sodium ions are depolarized with formation of sodium hydroxide and gaseous hydrogen.²⁰

6032. The electrodes of the Cowper-Coles generator²¹ consist of metallic sheets provided with tongues, which project downwards at an angle of about 45 degrees with the faces of the sheets. These electrodes are placed in separate collecting boxes or chambers, the liberated gases being guided into the latter by the inclined tongues of metal which project within openings in the sides of the

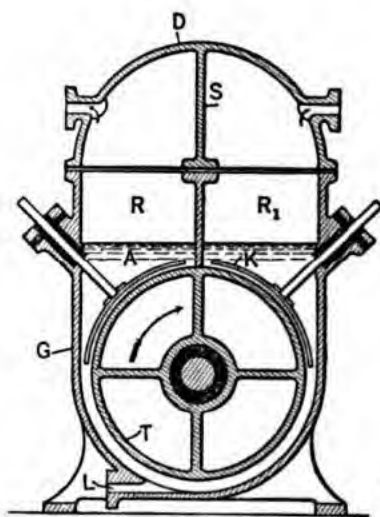


FIG. 217.

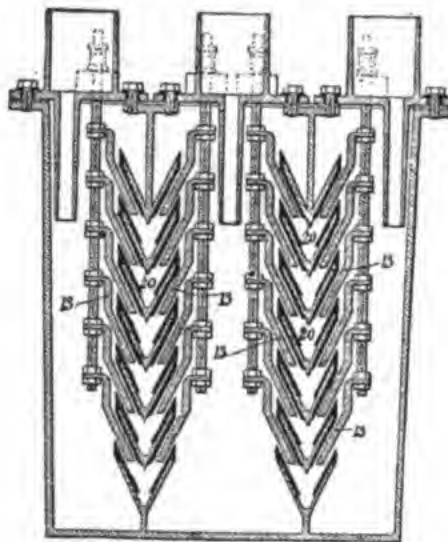


FIG. 218.

chambers. A battery of generators may be enclosed in a water jacket and provided with means for keeping the solution in each cell at a common level.

6033. With the object of completely preventing admixture of the two gases and at the same time keeping the electrical resistance low, Vaireille arranges the electrodes as shown in Fig. 218. Vertical rows of V-shaped troughs are provided with suitable insulation and serve to separate the positive and negative electrodes which are placed on opposite sides. The extremities 20 of these troughs are lower than the ends of the electrodes 13, so that the bubbles of gas coming from the latter cannot mix. The electrodes are both insulated from the container.²² In a modification, the troughs, described above, for the separation of the electrodes are replaced by vertical series of elements each of triangular section, and either solid or hollow. Each electrode consists of a sheet, with U-shaped pieces bound on each side with rivets. The gases are collected in bells, either stamped out of sheet metal or consisting of sheets cut out and folded, and united at the angles by autogenous soldering.²³

6034. Water is made more conductive, according to McCarty,²⁴ by the addition of tartrate of potassium, tartrate of sodium, or any of the citrates or other equivalents, and sul-

²⁰ Ger. Pat. 198,626, Nov. 13, 1906.

²¹ Brit. Pat. 14,285, Dec. 20, 1907.

²² French Pat. 355,652, June 27, 1905, and U. S. Pat. 823,650, June 19, 1906.

²³ First addition, Oct. 28, 1908, to French Pat. 355,652.

²⁴ U. S. Pat. 736,868, Aug. 18, 1903.

phuric acid. The apparatus ²⁵ consists of two tanks, connected by a pipe at about half their height. Each tank consists of an electrode, so located that the upper ends are about in a line with the axis of the connecting pipe, through which the current passes from one tank to the other. Each of the two tanks has an outlet at the top through which the gases generated may be led to suitable holders.

6035. Another apparatus ²⁶ consists of two receptacles, each containing one electrode and connected by a conduit near the bottom. Each electrode is a plate of platinum coiled upon itself a number of times and has a projecting terminal portion directly opposite the end of the conduit. In still another type ²⁷ the electrolytic cell is divided into two compartments by means of a solid diaphragm, which is perforated, short glass tubes being inserted in each perforation.

6036. Jaubert ²⁸ recommends a type of electrolytic hydrogen generator having electrodes covered by bells brought near to each other to diminish the resistance. The active surface of

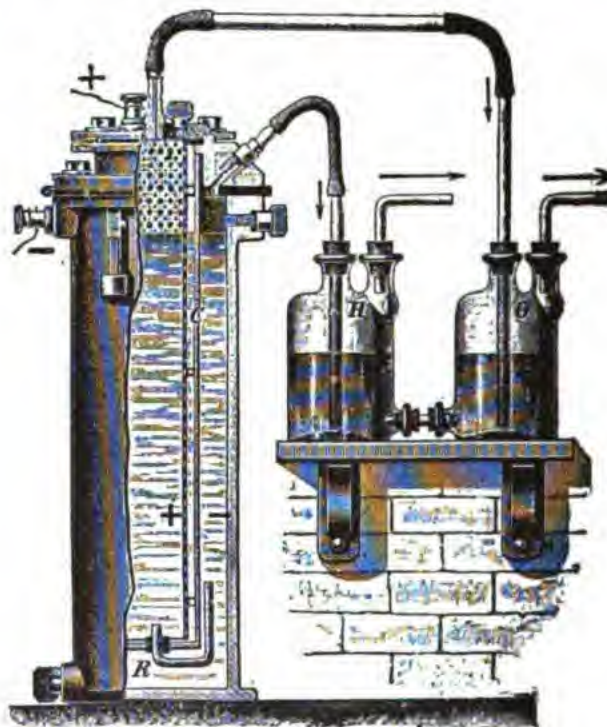


FIG. 219.

each electrode projecting below the lower level of the bell is inversely proportional to the volume of gas liberated at each electrode, while the volume of each bell is directly proportional to the volume of gas liberated. The bells are provided with cocks, or outlet collectors for the gases, and with insulated sleeves for the cables connected to the electrodes.

6037. Renard's apparatus for the generation of hydrogen is shown in Fig. 219. The container is made of cast iron and serves as the negative electrode. The cylinder *C* of asbestos material encloses the positive electrode, which is cylin-

²⁵ U. S. Pat. 721,068, Feb. 17, 1903.

²⁶ U. S. Pat. 816,355, Mar. 27, 1906, to McCarty.

²⁷ U. S. Pat. 814,155, Mar. 6, 1906, to McCarty; see also 813,105, Feb. 20, 1906.

²⁸ Brit. Pat. 102,974, Dec. 28, 1916; *J.S.C.I.*, 1917, 602; see also U. S. Pat. 1,255,096, Jan. 28, 1918.

drical in shape and is made either of iron or nickel. Through the bottom of the diaphragm cylinder the U-tube *R* establishes communication between the inner and outer vessels. The electrolyte is a solution made by dissolving 15 parts of caustic soda in 100 parts of water. Before the gases are passed to the gas holder they are led through the pressure equalizer marked *H* and *O*. With a current of 25 amperes at 3.5 volts a yield of 12 liters of hydrogen and 6 liters of oxygen

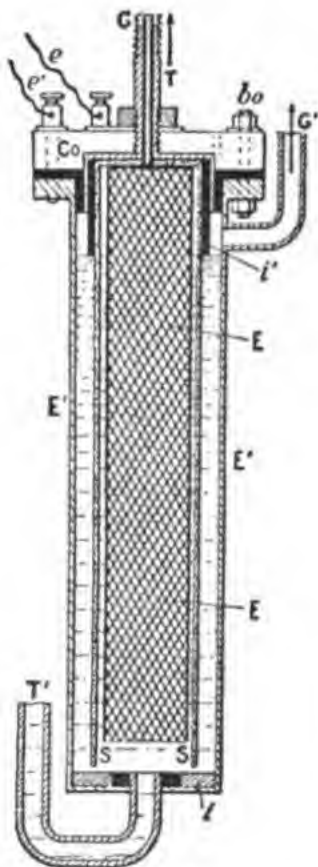


FIG. 220.

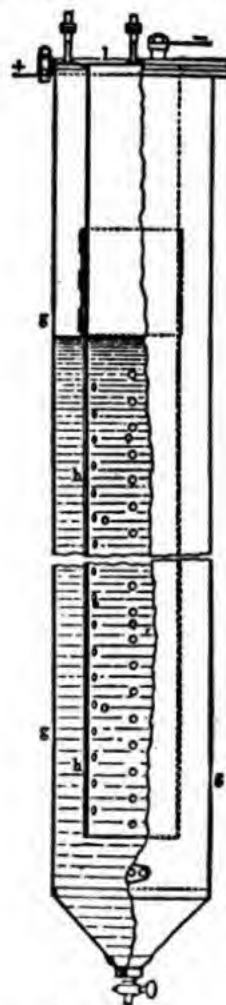


FIG. 221.

per hour is obtained. A form of construction of the Renard ²⁹ type is shown in Fig. 220 and also in Fig. 221.

6038. The apparatus of the Schuckert system ³⁰ is constructed, with the exception of the copper feed wires and the insulating material, entirely of iron. The cell proper of a unit designed to accommodate 600 amperes consists of a cast-iron trough (Fig. 222), approximately 26 in. long by 18 wide and 14 deep,

²⁹ Delmard, Ger. Pat. 58,282, Nov. 23, 1890.

³⁰ *Electrochem. Ind.*, 1903, 579.

requiring, when in operation, about 50 liters of electrolyte. In this trough are placed the iron electrodes. These are separated by strips of a good insulating material, extending from the top downward about three-fourths the depth of the cell. Between these separating plates and enclosing the electrodes are sus-



FIG. 222.—SCHUCKERT CELL.

pended iron bells, which collect and carry off the gas there generated. The electrolyte is usually a 20 per cent aqueous solution of pure sodium hydrate, although a 15 per cent solution may be used. The concentration is maintained by supplying to the cells an amount of distilled water equal to that decomposed

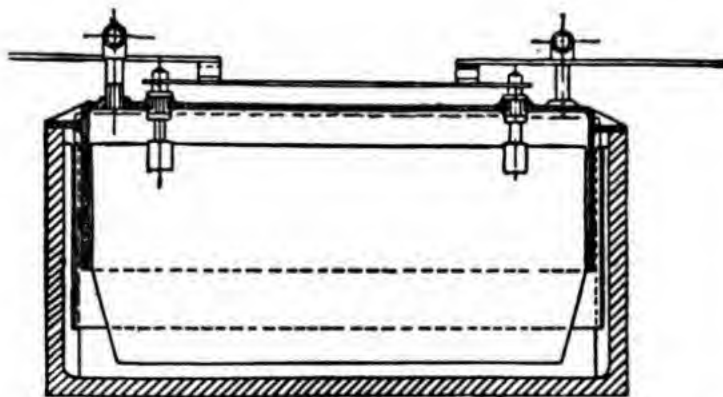


FIG. 223.—LONGITUDINAL SECTION OF SCHUCKERT CELL.

and carried away mechanically by the gas. The loss of sodium hydrate is inappreciable and may be entirely eliminated if the first wash water be used as feed water for the cells. The units may be connected either in series or parallel with a drop of potential between electrodes of from $2\frac{1}{2}$ and 3 volts. The apparatus is

operated most economically at a temperature of 70° C. When the cells are protected from radiation, as can be done, for example, by placing them on wooden boxes and packing them in one or two inches of sand, the heating effect of the passing current is sufficient.³¹

6039. The standard types of apparatus are designed to take from 100 to 1000 amperes, and to furnish gas at a pressure equal to water column of 70 to 80 mm. For special purposes a cell delivering gas sustaining a water column of 760 mm. may be secured. The production of normal types of apparatus is about 150 liters of hydrogen and 75 liters of oxygen per kilowatt-hour when measured over water at atmospheric pressure and at 20° C. The attention required for a plant of this kind consists simply in supplying the requisite amount of water to

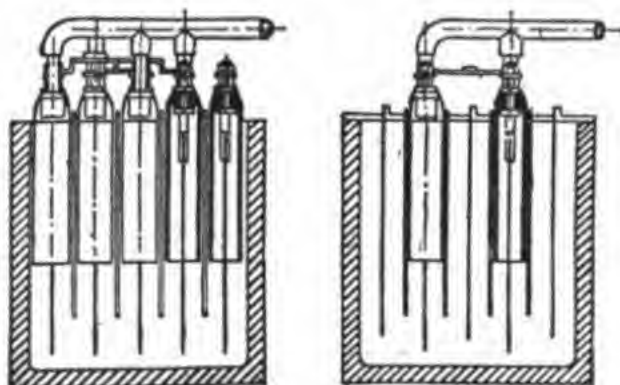


FIG. 224.—CROSS SECTION OF SCHUCKERT CELL.

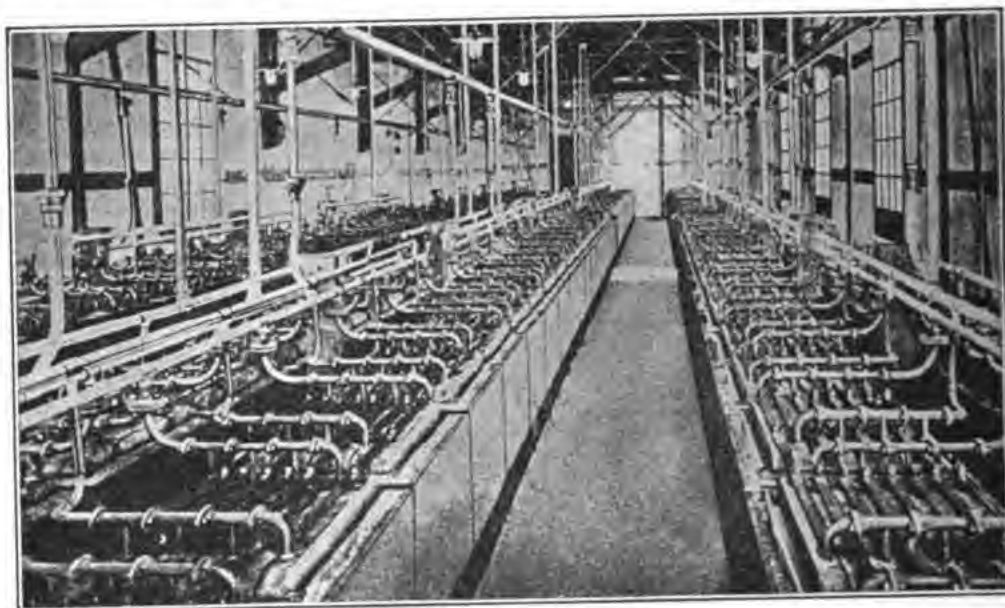
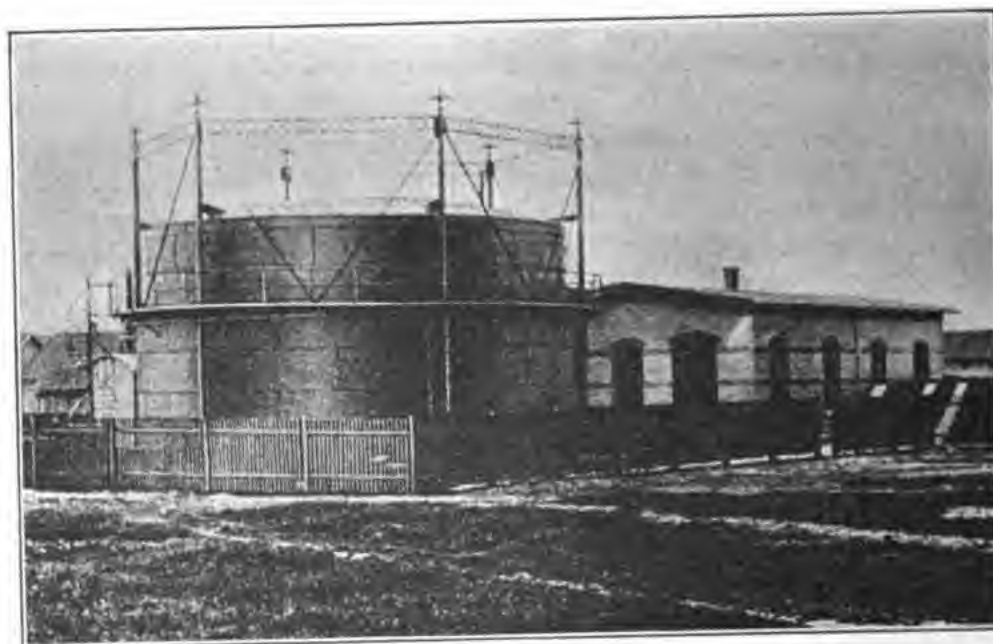
maintain the concentration constant. When in continuous operation the positive electrode, which is made up of a sheet iron plate two millimeters thick, should be replaced at the end of each year.³²

6040. Figure 225 shows the interior of a plant furnishing 1200 cu. m. hydrogen daily. Figure 226 shows the exterior of this plant. An equipment for an hourly production of 4 cu. m. hydrogen is shown in Fig. 227. Figure 228 is a compression room for charging cylinders with oxygen at 150 atmospheres pressure.

6041. A modified form of the Schuckert cell, as shown in Figs. 229 and 230, comprises a container tank, constructed of welded sheet iron and a number of positive and negative electrodes immersed in the solution. Eight separate bell castings are employed to house the electrodes and collect the gas as it is generated. These bell castings are made of a close-texture gray iron and are suspended from the top of the container tank by means of U-shaped steel supports. The container tank and the bell castings play no part in the operation of the generator and are insulated from the electrodes and all current-carrying metal. The electrodes are made of steel plates to each of which are welded two steel rods, both rods serving as terminals as well as supports for the electrode, holding it in position within the bell castings. The electrodes are alternately positive and negative. All of the positive electrodes are connected together by means of bus bars across the top of the tank and are led to a common

³¹ The Elektrizitäts-A.-G. Vorn. Schuckert & Co. have taken out German Pat. 231,545, Aug. 13, 1910, for the addition of soaps or soap-forming substances, preferably emulsified soaps, and of ferric oxide to the alkaline electrolyte employed.

³² See *Sci. Am. Suppl.*, 1913, 363.

**FIG. 225.****FIG. 226.**

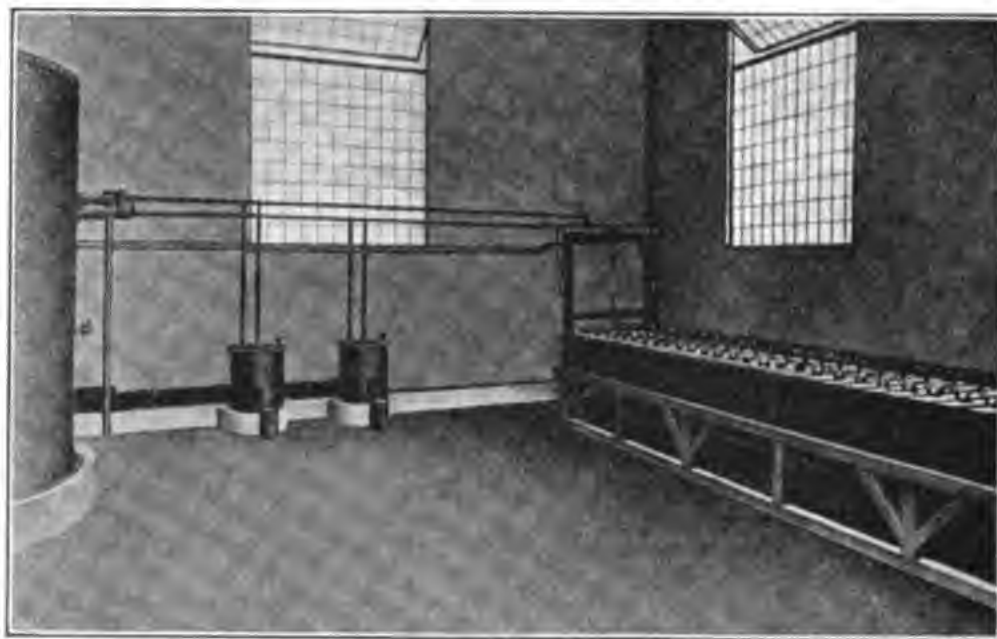


FIG. 227.

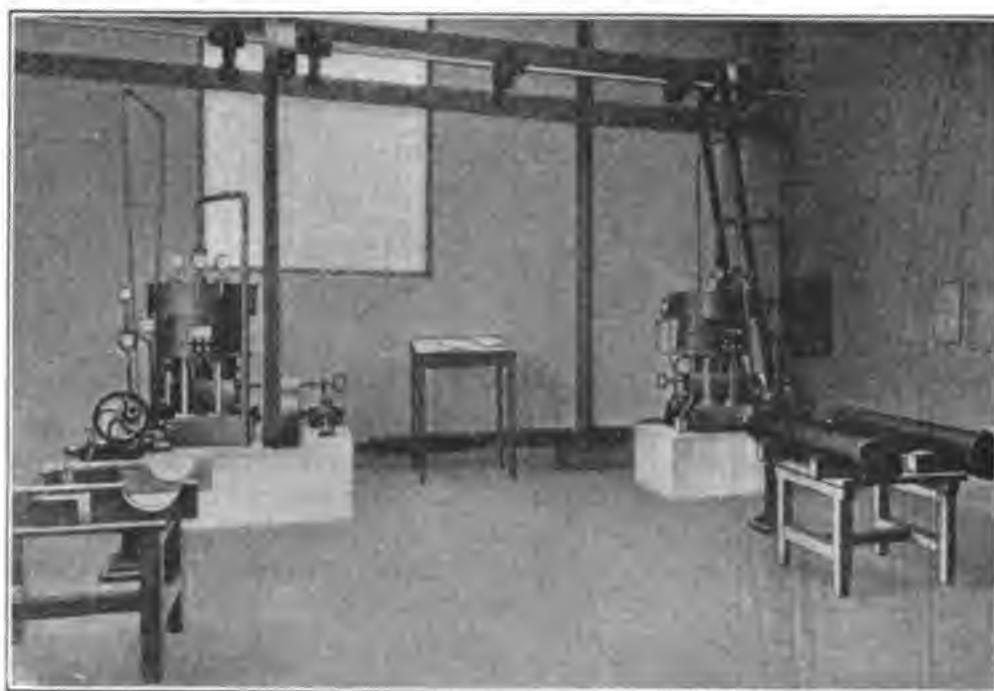


FIG. 228.

terminal. The negative electrodes likewise are connected together and led to a common terminal. Each bell casting is tapped for an eduction pipe to draw off the gas as generated. The four hydrogen pipes are connected together as shown and are led to the hydrogen pipe line connecting a battery of generators. The oxygen pipes are connected likewise. The electrolyte fills the container and owing to its height above the electrodes the gas is generated under an appreciable pressure amounting to approximately 1 lb. per square inch.

6042. The novelty that distinguishes the Schuckert cell from the majority of other generators is the absence of any diaphragm in the construction. While a diaphragm is actually not used, still the sides of the bell castings act in the capacity of a diaphragm to prevent the mixing of the gases.

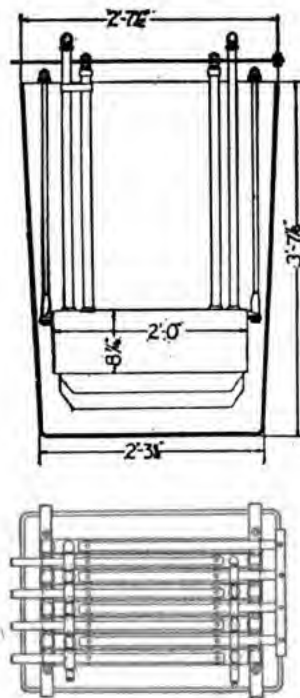


FIG. 229.



FIG. 230.

6043. The working efficiency of the Schuckert cell under normal conditions of temperature is said to average from 4.5 to 5.5 cu. ft. of hydrogen per kilowatt-hour of electricity passed through it. Or, in other words, the voltage required to force 400 to 600 amperes through each cell will vary from 2.9 to 3.5 according to the condition of the plant. Too high an amperage results in so rapid an evolution of gas that there is a tendency under these conditions for the gas in one chamber to be forced down and under the wall of the next partition which, of course, will result in mixed gas or the escape of gas into the generator room.

6044. Another difficulty said to be met with in operating under high amperage is the wearing away of the anode, charging the electrolyte with small particles of iron compounds which show a tendency to be attracted to the cathode and gradually form a deposit. These accretions have been known to build across the space between the electrode and the bell castings causing short-circuiting and

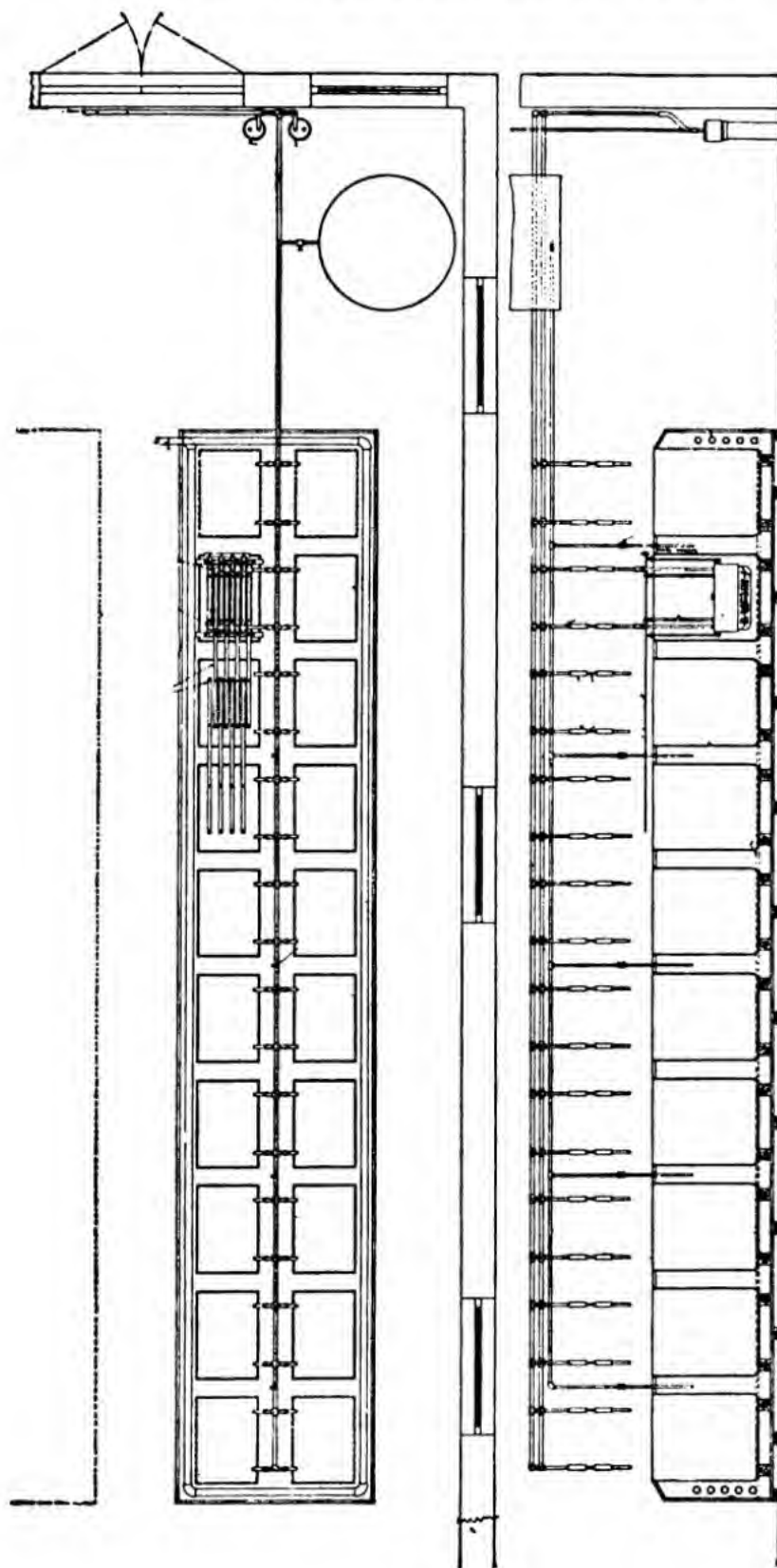


Fig. 231.—OXYGEN-HYDROGEN PLANT. Schuckert type.

permitting the bell castings to become charged, with consequent evolution of gas on its outer side and the escape of gas into the generating room.³³

6045. The Burdett system³⁴ of electrolytic apparatus consists of a varying number of generators or units, connected electrically in series. The unit, Fig. 232, comprises a container enclosing the electrodes and electrolyte, but the walls of the container do not function as electrodes. It is usually mounted on concrete foundations and is insulated both from the ground and from the generator proper. The electrodes are arranged on the multiple system, there

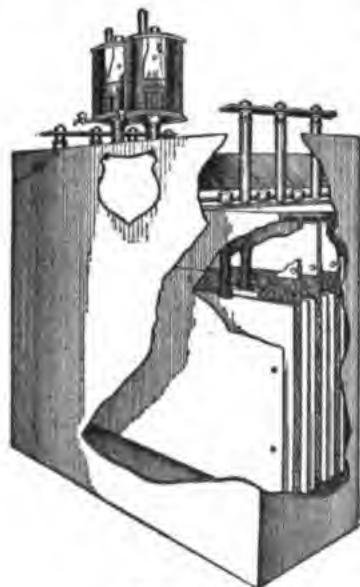


FIG. 232.

being a number of both positive and negative electrodes in each unit. The electrodes are separated from each other by a partition of specially prepared asbestos cloth which under the conditions of operation is permeable to the solution but not to gas. A bell or box casting, open at the bottom, is used for housing the electrodes and the asbestos diaphragm is stretched across the box casting from one side to the other, forming a number of compartments. In each of the compartments an electrode is placed running parallel to the asbestos curtain or diaphragm. The electrical connections are so arranged that commencing with and including the first electrode, every other electrode is a cathode, the alternate electrodes being anodes. At the top of the container the electrode terminals are joined by means of copper bus bars, thus bringing all the anodes to a common anode terminal and all of the cathodes to a similar connection.

6046. The gas generated at the electrodes rises and is collected in the separate gas-tight compartments. These compartments are joined by two cored gas passages in the bell casting and the gases pass through these passages into and through glass indicators and purgers to the gas mains. Inserted in each of the service mains is a gas meter, a flash-back, and a water purger which removes the water held in suspension in the gas and at the same time acts as a pressure regulator for the generators. Purifiers are usually inserted in each line to cleanse the gas. The hydrogen and oxygen are led to their respective gasometers and from there are compressed into storage tanks for use. By means of controls the compression may be taken care of automatically.³⁵

³³ The Schuckert apparatus is supplied by the Elektrizitäts-A.-G. Vorm. Schuckert & Co., Nürnberg. In a private communication they state that an electrolyzer battery, capable, when running at a temperature of 50° to 60° C., of producing hourly 10 cu. m. of hydrogen, yields the gas of 99.5 per cent purity.

The temperature of the electrolyzer room should be maintained at least at 15° C. In cold weather it must be heated. An electrolytic hydrogen and oxygen generator of the bell-collector type is described by Benker (*J.S.C.I.*, 1914, 256, and French Pat. 461,981, Aug. 29, 1913).

³⁴ U. S. Pat. to Burdett, 1,086,804, Feb. 10, 1914.

³⁵ The author is indebted to Mr. Paul Pleiss for a description of the Burdett generator, also for some data on the Garuti and Schuckert cells.

6047. The automatic control feature of the Burdett apparatus is useful. By means of electrical regulating devices the entire electrolytic equipment is under automatic control. It also serves as a safety device, preventing over-generation of gas or undue pressure on any parts of the apparatus. The compressor, when the collecting gasometer reaches a predetermined height, will auto-

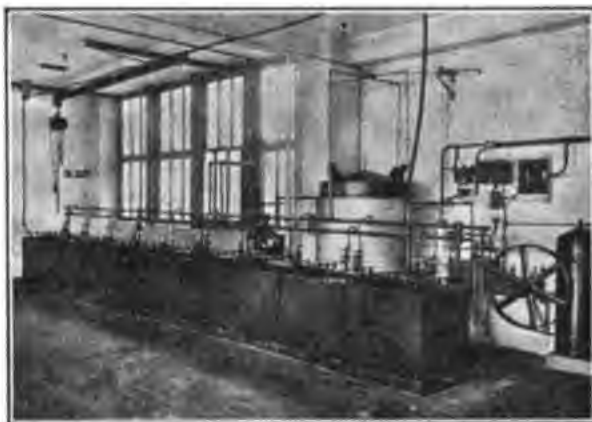


FIG. 233.

matically start, and will stop when the gasometer falls to a predetermined level. Electric control is provided which will stop the motor of the compressor when the storage tank pressure reaches a certain point, starting the motor when the pressure falls again, and another control is provided which will stop the generation of gas when both gasometer and storage tank are charged to their full capacity.



FIG. 234.

6048. Figure 233 shows a battery of Burdett generators and Fig. 234 illustrates a complete equipment embracing motor-generator, gasometers, storage tanks and automatic control devices. Each generator operating under a current of 400 amperes will produce in excess of 6 cu. ft. of hydrogen and one-half this amount of oxygen per hour, or in round numbers,

150 cu. ft. of hydrogen and 75 cu. ft. of oxygen per 24-hour day with the gas measured at 20° C. and 760 mm. It is desirable to operate the plant as continuously as possible and a run of twenty-three or twenty-four hours per day is recommended. Each cell operating under normal conditions will require, with a solution temperature of 80° F. about 2 volts for the passage of 400 amperes. Thus each cell requires about 800 watts (0.8 kilowatt-hour) per hour to produce about 6 cu. ft. of hydrogen per hour. The efficiency of the generator is therefore high. If the cell generator be artificially heated the consumption of electricity may be decreased by about 10 per cent with a corresponding increase in the efficiency of the unit. The hydrogen will average in purity 99 per cent or higher.

6049. Electrolytic apparatus designed by Hazard-Flamand ³⁶ is shown in Fig. 235. Between the inner and outer electrodes a porous diaphragm is inserted

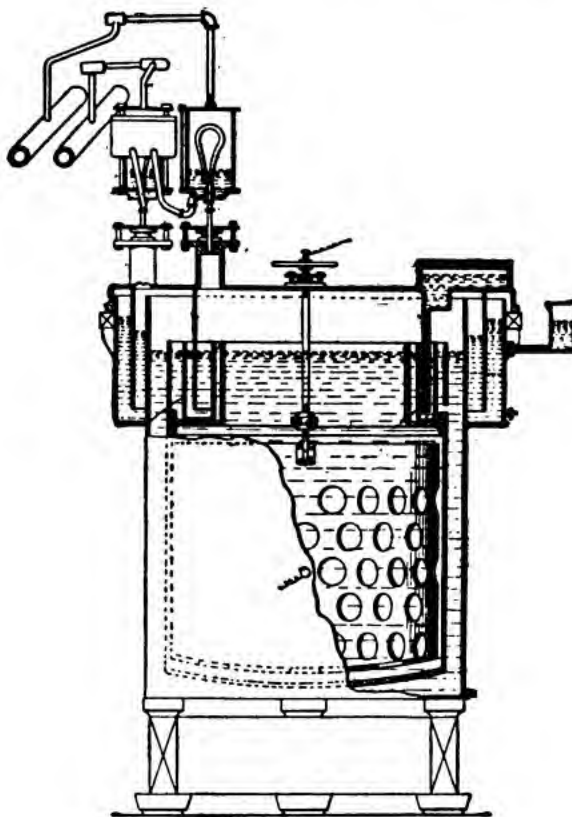


FIG. 235.

and a fluid seal is disposed about both sides of the top of the diaphragm and is composed of an outer seal and an inner seal, consisting of two concentric troughs one within the other. The electrolyte is fed into the inner trough, passes to the outer trough and is delivered from the latter on both sides of the diaphragm.³⁷

6050. One form of electrolytic cell which found considerable use (International Oxygen Company apparatus) is very simple, an outside view being given in Fig. 236 and a diagram in Fig. 237. The iron tank or container serves as the cathode, being connected to the negative pole of the electric supply

³⁶ U. S. Pat. 1,003,456, Sept. 19, 1911, assigned to the International Oxygen Co.

³⁷ See also U. S. Pat. 646,281, Mar. 27, 1900, to Hazard-Flamand.

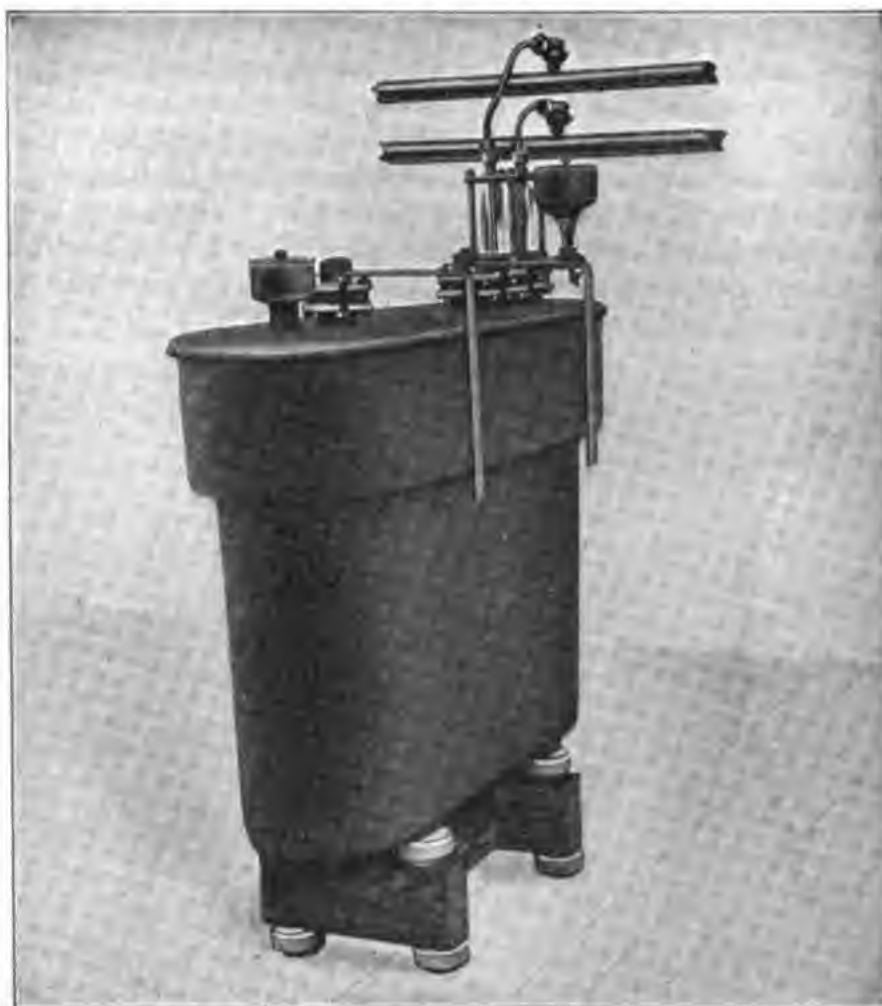


FIG. 236.

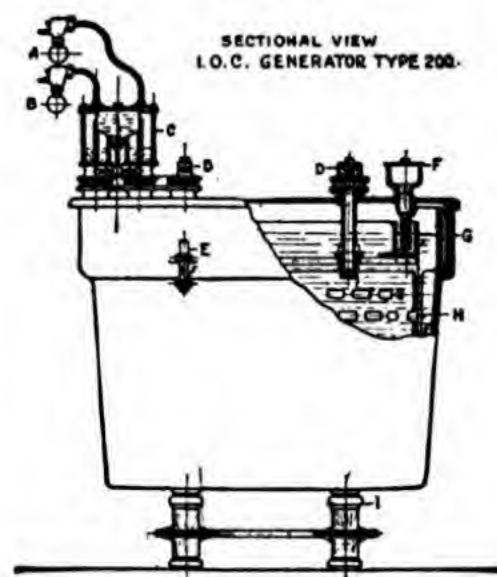


FIG. 237.

circuit. From the cover of this tank is suspended a perforated tank which serves as the anode, being connected to the positive pole of the supply circuit. It is made of a specially selected low-carbon steel, to prevent the formation of spongy rust. By means of an asbestos sack, suspended from the cover between anode and cathode, two separate compartments are formed. At the top these compartments are sealed by a hydraulic joint. Through an opening in the cover a solution of caustic alkali in distilled water is poured into the hydraulic joint and distributed in the two compartments. The whole cell is placed on insulating supports of porcelain.

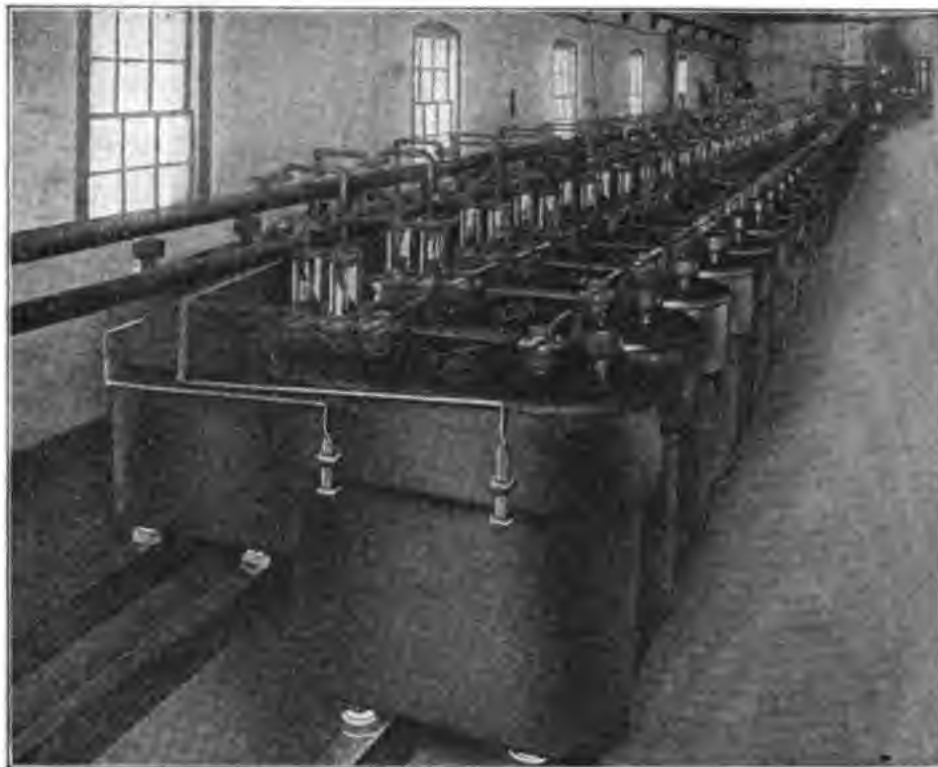


FIG. 238.—BATTERY OF I. O. C. GENERATORS.

6051. The oxygen and hydrogen gases evolved do not pass directly from their compartments to the offtake pipes, but first bubble through water contained in the two "lanterns" on top of the cell. This enables the operator to see at a glance how the cell is working. The purity of the gases produced is very high. A sample of hydrogen produced by this electrolyzer, analyzed by the Conservatoire National des Arts et Métiers in Paris, showed 99.70 per cent hydrogen.

6052. All that is required for the operation of the cell is the daily addition of somewhat over a gallon of distilled water to make up for the quantity decomposed into hydrogen and oxygen. The daily output is approximately 72 cu. ft. of oxygen and 144 cu. ft. of hydrogen. As to the electrical energy requirements

a joint test ³⁸ made in November, 1910, by the Laboratoire Centrale de l'Electricité and the Conservatoire National des Arts et Métiers with two unit cells of this type of electrolytic cell showed that the production of 1 cu. ft. of oxygen and 2 cu. ft. of hydrogen requires 0.2797 kilowatt-hour. Reversely 1 kilowatt-hour produces 3.54 cu. ft. of oxygen and 7 cu. ft. of hydrogen. Each unit cell requires a little above 2 volts and from 300 to 400 amperes. A current of 350 amperes produces about 65 cu. ft. of oxygen and 130 cu. ft. of hydrogen per day.

6053. The following table gives the results of a test made by the Electrical Testing Laboratories of New York for the International Oxygen Co.

Cell No.	Average am-peres	Average volts	Average watts	Maximum temp.	Purity of oxygen	Cubic feet per hour		Cubic feet per kilowatt-hour	
						Oxy-gen	Hydro-gen	Oxy-gen	Hydro-gen
8.	405.1	2.388	967	31.8° C.	97.73%	3.247	6.184	3.358	6.395
14.	405.0	2.562	1038	30.0° C.	98.67%	3.239	3.120
66.	368.8	2.826	1042	32.0° C.	98.46%	2.886	5.788	2.770	5.555
70.	392.0	2.660	1043	26.5° C.	98.50%	3.082	6.254	2.955	5.900
Average..	392.7	2.609	1022	30.1° C.	98.34%	3.114	6.075	3.051	5.950

The four cells tested were selected as being representative of the entire battery after taking a set of preliminary electrical measurements on each of the cells. All of the data given are from readings as actually observed and corrected for instrument errors. Gas volumes are corrected for moisture and calculated to 20° C. and 760 mm.

6054. One of the objections advanced against the electrolytic system is the relatively large floor space which it occupies, and to obtain an apparatus of a durable yet compact character the author, many years ago, designed a generator having T-shaped ribs on both anode and cathode, affording a large generating surface without excessive bulk. Figure 239 shows a form of anode and Fig. 240 the assembled generator.³⁹ The sectional type of apparatus (see paragraph 6026) represents a more effective solution of the problem of securing greater compactness.

6055. An electrolytic hydrogen and oxygen generator with cobalt as the active anode element and iron as the cathode has been developed by Levin.⁴⁰ The generator unit consists of a rectangular thin iron plate casing of small height, long and narrow. Any number of these may be joined together to form a complete generator. The iron casing is divided into two parts by an asbestos diaphragm, suspended from an impermeable partition which reaches about one-fourth of the way down into the cell from the top. An electrode is placed in each compartment formed by the diaphragm. The partition in the upper part of the cell prevents the combination of oxygen and hydrogen after these gases have been generated and have risen separately to the top of the cell, being prevented from mixing by the diaphragm. Suitable means are provided for carrying away the gases, filling the generators with electrolyte,

³⁸ *Met. and Chem. Eng.*, 1911, 471.

³⁹ U. S. Pat. 1,087,937, Feb. 24, 1914, to Ellis.

⁴⁰ *Met. Chem. Eng.*, 1917, 401; U. S. Pat. 1,214,934, Feb. 6, 1917; Brit. Pats. 102,933 and 108,477, application date Oct. 27, 1916.

etc. The anode is made of iron, electroplated with a thin film of cobalt, and the cathode is of iron, preferably electrolytic. The electrodes are given a previous treatment by making them the anode in a solution of a salt of the active surface metal, and electrolyzing for a brief period. This is claimed to give greater efficiency in operation.

6056. An electrolytic gas generator devised by Levin ⁴¹ is provided with electrodes entirely independent of the container or casing. The casing is divided into three compartments, in each of which an electrode is located. The cell is of the sectional type so that a number of units may be assembled in a compact manner. The electrode compartment of the

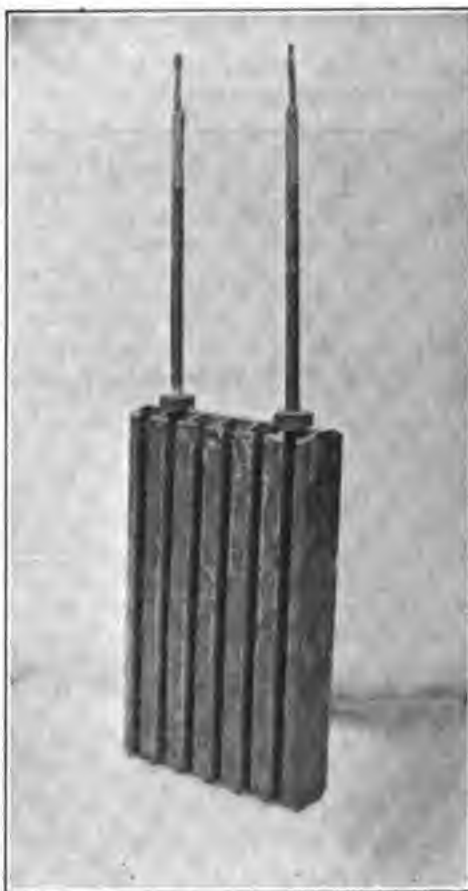


FIG. 239.

generator has a gas outlet which is sealed with water, and through which water is supplied to the compartment, from a chamber above. The water chamber is provided with a gas outlet and a water-supply conduit.⁴²

6057. A form of Levin generator (Electrolytic Oxy-Hydrogen Laboratories, Inc. or Electrolabs), has been built of a few standardized parts which can be rapidly assembled. The generator consists of three compartments. The oxygen is generated in the two outer compartments and the hydrogen in the center compartment. Two sheet-metal frames, to each of which is attached an asbestos

⁴¹ U. S. Pat. 1,219,966, Mar. 20, 1917.

⁴² See also U. S. Pat. 1,247,694, Nov. 27, 1917; and 1,199,472, Sept. 26, 1916, to Levin; *Chem. Abst.*, 1918, 253; Can. Pat. 175,807, Mar. 20, 1917; *Chem. Abst.*, 1917, 3001.

diaphragm, serve as the separating mediums. The electrodes are independent of the casing. They are separated from and securely fixed within the casing by specially designed blocks of asbestos. The surfaces of both the anode and cathode are plated. The use of cobalt for such purpose is one of the features of this generator. Each compartment has an independent water feed which also serves the purpose of a blow-off device to vent the gas from each compartment under



FIG. 240.

abnormal conditions. A specially designed sight-feed indicator is placed between the generator and the gas offtake pipe. Each indicator makes the generating unit to which it is attached independent of all the other generators in the group. It further serves to keep uniform the pressure of the oxygen and hydrogen inside the individual generator. It also enables one to see at a glance whether the gases are being generated properly. The generator is welded throughout. The

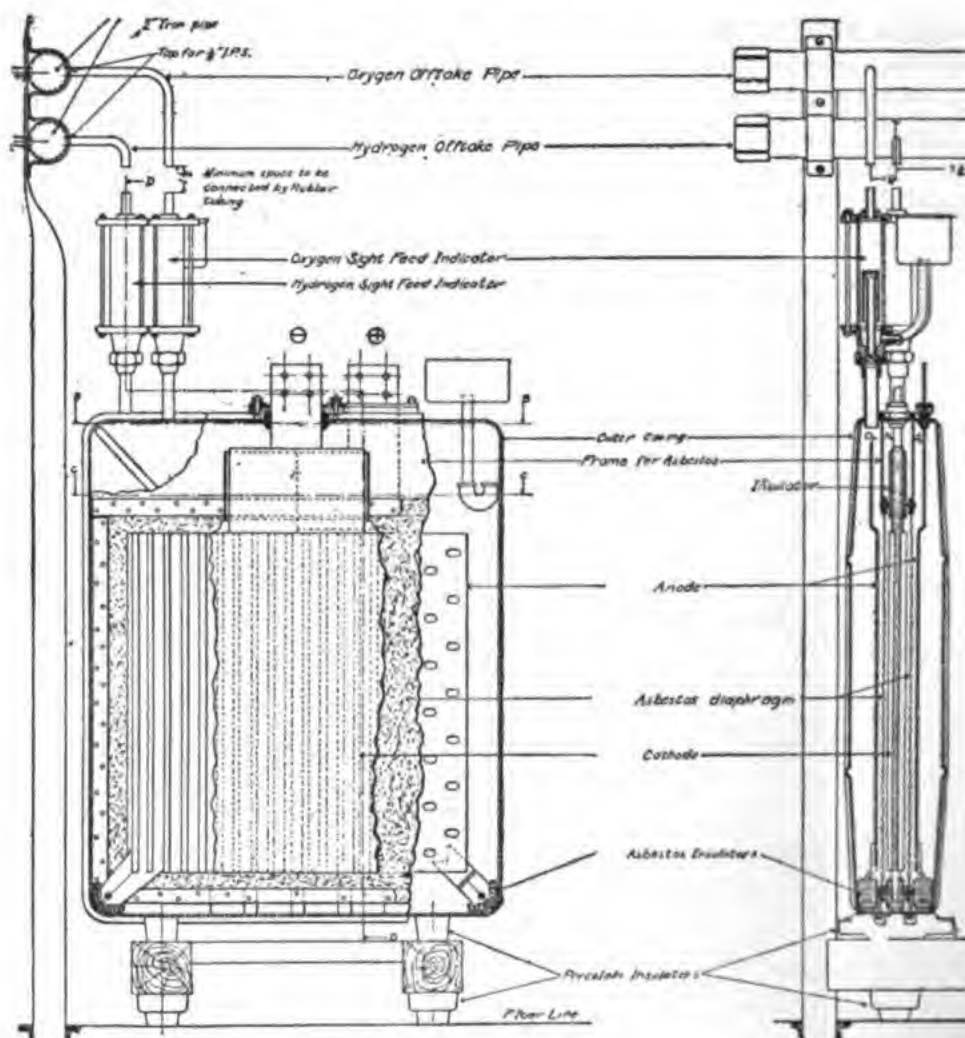
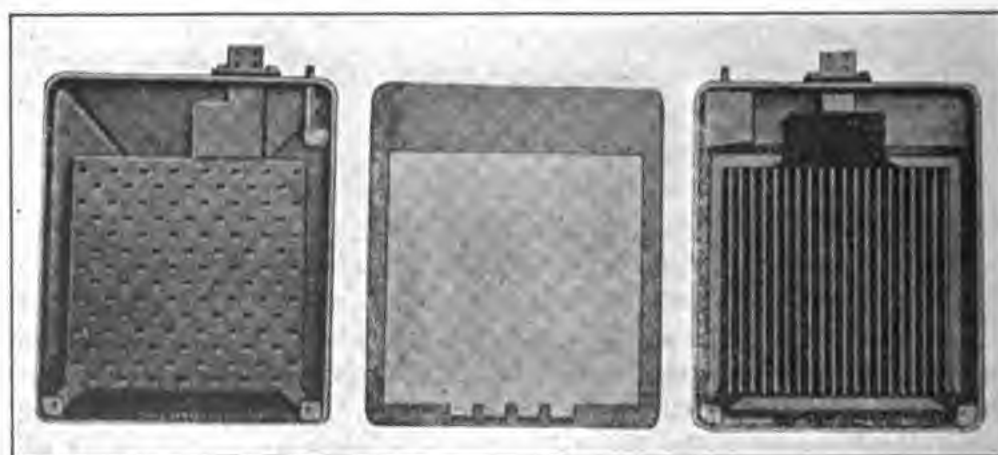


FIG. 241.



Anode Compartment.

Asbestos Diaphragm.

Cathode Compartment.

FIG. 242.

dimensions of the unit are $30 \times 25 \times 6\frac{1}{2}$ in. The construction is shown by Figs. 241 and 242. Figure 243 shows the assembled unit and Fig. 244 is a group of generators.

6058. In a day of 24 hours this form of Levin generator at 200 amperes will produce 38.4 cu. ft. of oxygen and 76.8 cu. ft. of hydrogen, measured at 20°C . and 760 mm. pressure. A battery of 100 generators will occupy a space 31 ft. long by 4 ft. 6 in. wide and will produce:

In 1 hour	160 cu. ft. oxygen
	320 cu. ft. hydrogen
In 24 hours	3840 cu. ft. oxygen
	7680 cu. ft. hydrogen

Each generator running at 200 amperes requires slightly over $\frac{1}{10}$ kilowatt per hour. In a space 31 ft. \times 4 ft. 6 in. and with a normal room height (10 to 12 ft.) 200 Levin generators can be installed in two tiers.

6058A. An electrode devised by Levin for use in unipolar cells consists of parallel metallic plates immersed in a tank containing the electrolyte, and insulated from the tank, which itself forms the other electrode. The plate electrode is connected at a number of evenly disposed points on its surface with one of the current mains by a number of leads passing between the plates, while the tank is connected with the other main by a band of highly conducting metal surrounding it at about half its



FIG. 243.

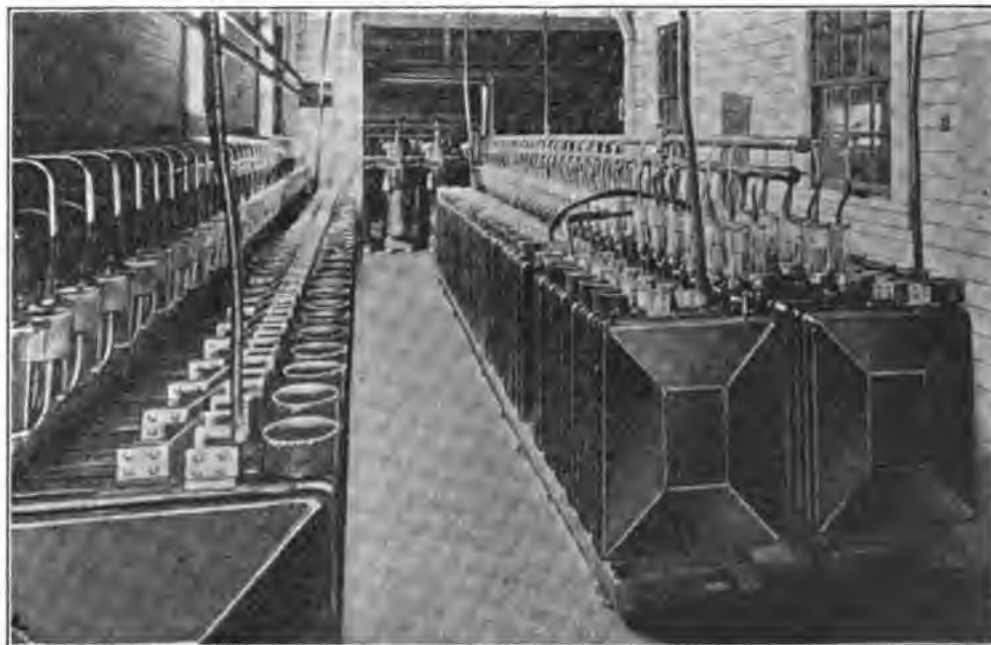


FIG. 244.—ELECTROLABS (LEVIN) GENERATORS.

height. In this way unequal distribution of the current throughout the electrodes is prevented and uniform generation of gases at different portions of the surfaces ensured.⁴³

6059. Griffin's apparatus for generating hydrogen and oxygen by electrolysis⁴⁴ consists of a cell and a plate of conducting material depending into water of each cell. This plate is bent just above the cell and is attached to the adjoining cell, thus making a continuous flow of current from one cell to the next. The plate is enclosed in a sack of asbestos to separate the oxygen and hydrogen. The asbestos sack may be spaced from the plate by some insulating material to insure a complete separation of the gases. (See Fig. 245.)

6060. Kato states that in the electrolytic preparation of hydrogen and oxygen,⁴⁵ the diaphragms used in the commercial apparatus do not keep these gases completely separate, as shown by diffusion data given. Kato finds that

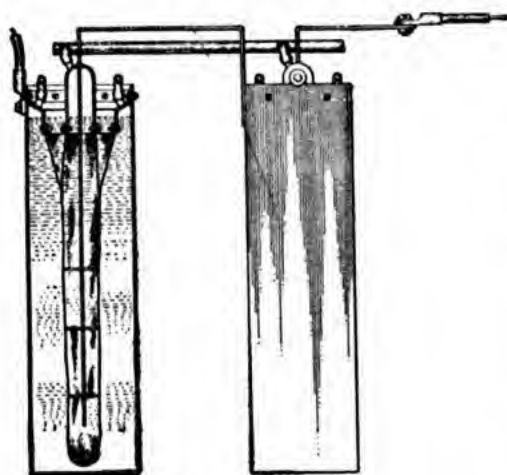


FIG. 245.

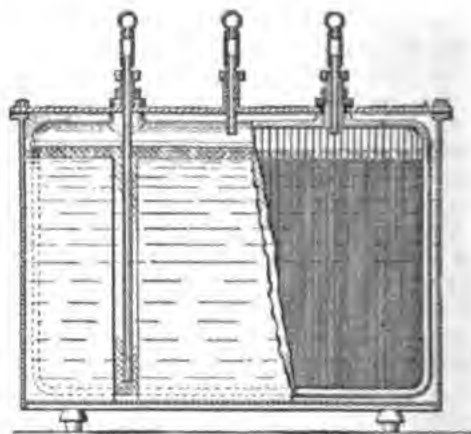


FIG. 246.

pure gases can be technically prepared without the use of a diaphragm. Special electrodes are employed which have an inclined active surface to which the generated gas adheres by reason of its buoyancy and accordingly does not diffuse into the solution.

6061. Halter has devised an electrolytic cell⁴⁶ (see Fig. 246) for the production of oxygen and hydrogen in which a tank, acting as the cathode, is provided with a cover, from which the anode constructed of wires united in the form of a hollow body, is suspended in the electrolyte.

6062. A separator, of porcelain or other non-conducting and oxygen-resisting material, is supported over the anode with its sides extending below the surface of the electrolyte, and the closed top is provided with an oxygen outlet. An asbestos sack is secured to and suspended from the separator, enclosing the anode below the surface of the liquid, the separator and sack constituting a complete non-conducting enclosure for the anode. Means are provided for conducting off the hydrogen from the space beneath the cover of the separator.

⁴³ U. S. Pat. 1,481,648, Jan. 22, 1924.

⁴⁴ U. S. Pat. 1,117,185, Nov. 17, 1914.

⁴⁵ *J. Chem. Ind.*, Japan, 1915, 18, 919; *Chem. Abst.*, 1916, 561.

⁴⁶ U. S. Pat. 1,172,885 and 1,172,887; *J.S.C.I.*, 1916, 476.

The tank is made in the form of a narrow upright chamber, with a partition dividing the interior of the tank into narrow vertically arranged compartments, the partition and walls of the tank forming the cathode. Each anode is formed from spaced perforated sheet-metal plates, arranged so as to have a hollow oblong form in horizontal section, with curved ends and bottom and secured at its upper edges to a horizontal conducting bar supported from the cover of the tank. A separator of non-conducting material, with attached sack enclosing the anode, is inverted over each anode and disposed lengthwise in the chamber. The partition is formed from two plates, back to back, with their end portions curved apart and around the ends of the anodes.



FIG. 247.



FIG. 248.

6063. The Davis-Bournonville Company system of hydrogen and oxygen generation embraces an electrolyzer of a compact type, shown in Fig. 247. The electrodes of this apparatus are of sheet metal, the anodes being nicked.⁴⁷ An alkaline electrolyte is used. The electrolyzers have been made in two sizes, 500 and 1000 amperes, with a hydrogen output of 7.92 and 15.84 cu. ft., respectively. Figure 248 shows an anode of a 1000 ampere electrolyzer. A Swartley

⁴⁷ Swartley, U. S. Pat. 1,263,959, April 23, 1918.

hard-rubber separator ⁴⁸ (Fig. 249) is shown at the base of the anode. The separator is an inverted trough-shaped structure which is disposed over each anode member and extends a short distance below the surface of the electro-



FIG. 249.—SWARTLEY SEPARATOR.

lyte. The separator supports an asbestos sack which covers the anode member and serves to confine the oxygen. The container and partition, Fig. 250,

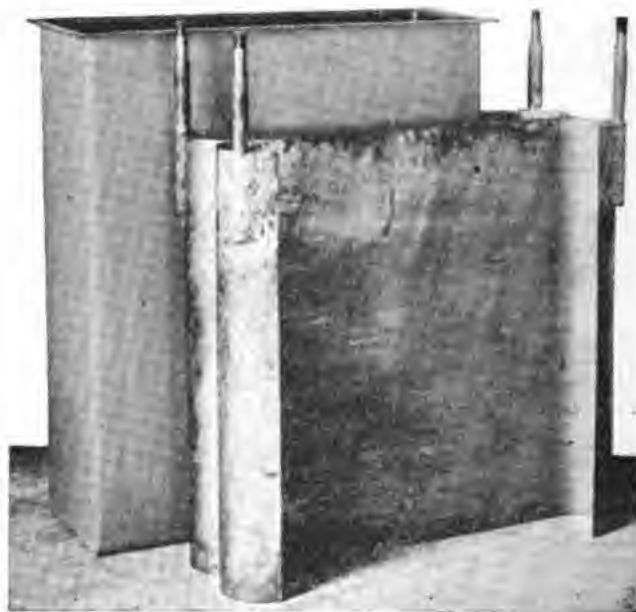


FIG. 250.

constitute the cathode element. Figure 251 shows the method of assembling of anodes on the cast-iron electrolyzer cover, one anode being enclosed in an asbes-

⁴⁸ U. S. Pat. 1,176,105, Mar. 21, 1916.

tos sack. Figure 252 shows a typical arrangement of fifty of the 500 ampere electrolyzers.⁴⁹

6064. Jones⁵⁰ has designed an electrolytic cell for the production of hydrogen and oxygen. The apparatus is provided with a number of electrodes, and



FIG. 251.—ASSEMBLING THE ANODE PARTS.

a diaphragm between adjoining electrodes forms chambers for the separation of the evolved gases, with gas ducts leading from them and separate conduits connected with the gas ducts. The electrolyte is conveyed to the several chambers by supply ducts connected to a supply conduit, the various conduits being

⁴⁹ This type of apparatus has been made under the Bucknam Pat. 1,172,932, Feb. 22, 1916. A description of the Davis-Bournonville equipment is found in *Oxy-Acetylene Welding* by Miller, New York, 1916, 30.

⁵⁰ U. S. Pat. 1,212,229, Jan. 16, 1917; *J.S.C.I.*, 1916, 391.

located beyond the electrodes, and so arranged as to be outside the path of the electric current through the apparatus.

6065. Mueller and Rowlands ⁵¹ describe a water electrolyzing apparatus made as follows:

A tank (Fig. 253) is made in two sections, a lower and an upper section, electrically separated by an insulating joint formed by a trough extending around the top of the lower section and containing a U-shaped insulating gasket of soft rubber which forms a cushion and also a hermetic seal. A liquefiable insulator such as paraffin filling the upper portion of the trough further insures a tight joint between the sections. The lower edge of the upper section rests in the groove of the gasket. The interior of the lower section is divided by lon-

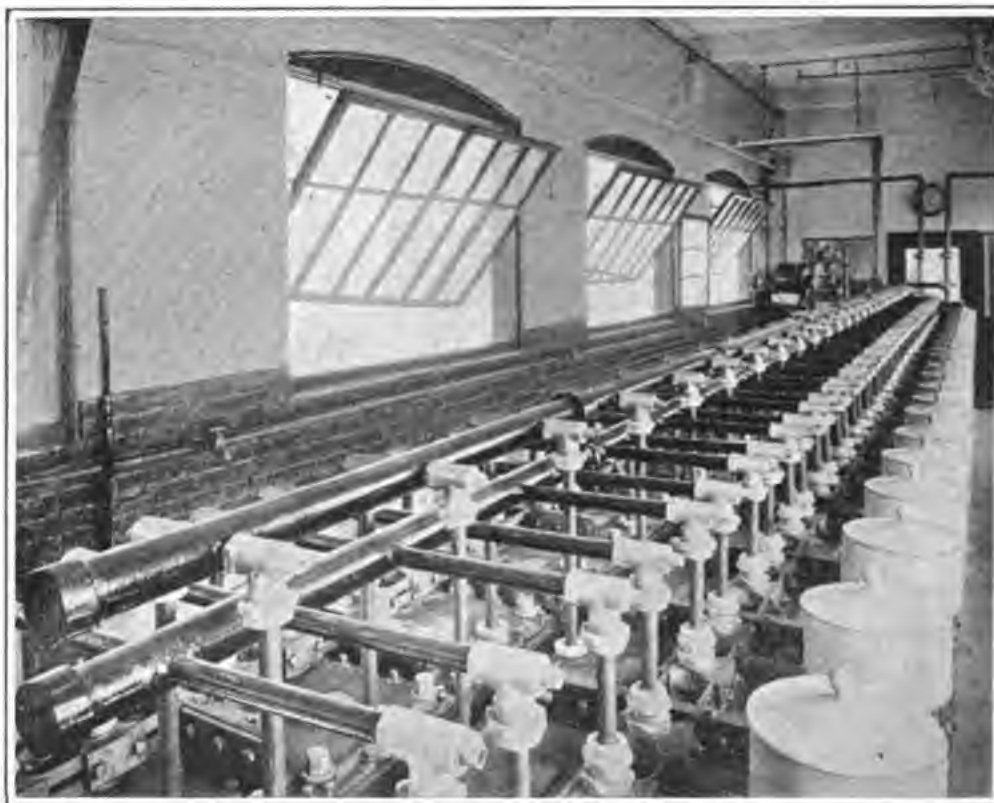


FIG. 252.

gitudinal webs parallel with the side walls, into equal-sized cellular spaces which are open at top and bottom, these webs extending only from the upper edge of the section to the top of the enlarged base. The webs are perforated at intervals with holes.

6066. The anodes (three in number) are disposed in the spaces between the webs and side walls of the section thus exposing a double surface to the electric current for each anode, and hang in diaphragms of woven asbestos. The lower section is the negative electrode, while the upper section is insulated from both electrodes and is designated the neutral section. The anodes are suspended from the cover, which in turn rests upon the neutral section but is insulated therefrom by means of a grid-shaped rubber gasket. To insure gas-tight joints between the hydrogen and oxygen chamber, and for sealing both chambers from the outer air, the neutral section is provided with a series of parallel inner troughs for the former, and for the latter

⁵¹ U. S. Pat. 1,220,262, Mar. 27, 1917.

is provided with an encompassing outer trough in which the depending marginal flange of the cover is sealed by paraffin wax or pitch. The diaphragms each consist of two parts, the diaphragm proper and a hanger. The hanger is made of thin sheet metal, and obviates the necessity of rendering gas-impermeable that portion of the diaphragm which extends above the liquid level. It is tubular in form, of the same cross-section as the diaphragm and of sufficient length to extend below the liquid level. It is formed at its upper end with an outwardly and downwardly projecting flange of proper form to fit into the sealing trough which extends continuously around each hanger. The cell represents a highly elaborated form of water electrolyzing apparatus, the complete details of which cannot be presented here.

Another form of apparatus designed by Mueller and Rowlands⁵² consists of a deep metal tank divided into communicating compartments by vertical partitions which form, with the sides, a series of electrodes of the same polarity. The tank has an arched metal cover from which depends a number of metal plates, one nearly to the bottom of each compartment, forming a corresponding series of electrodes of opposite polarity. The cover is insulated from the tank by a diaphragm, through openings in which the metal plates extend; and each plate is surrounded by a tube of flexible, non-corrodible material.⁵³

6067. An apparatus described by Lane,⁵⁴ has the vertical edges of the flanges of a vertical plate of substantially channel-shaped cross-section welded to the line of fold of the succeeding similar plate so as to form a bell or funnel for the collection of gases evolved during electrolysis.

6067A. Another modification of electrolytic cell involves the use of flat parallel electrodes joined by current leads made of nickel-plated copper strips.⁵⁵

6067B. Electrode corrosion is stated to diminish in the order: nickel steel, cobalt steel, steel, nickel-plated steel, nickel. Corrosion is marked with alkali carbonate solutions. The cathode over-voltage is lowest with nickel and with rough surfaces. As electrolyte 20 per cent sodium hydroxide solution is preferably employed with an asbestos diaphragm.⁵⁶

6068. In a form of electrolytic cell for obtaining hydrogen and oxygen, described by Churchill & Co., and Geeraerd,⁵⁴ a vertical series of inclined non-conducting vanes are arranged close to the electrodes to confine gas flow to the space between the vanes and the electrodes.

6069. Electrolysis under High Pressure. In an article by Noeggerath⁵⁵ an account is given of an electrolytic generator which delivers the gases under high (150 atmospheres) pressure, with high efficiency. Considerable economies result from this method owing to the elimination of compressors. Moreover the cost of housing is saved because the generators work perfectly well out of doors.

6069A. An electrolyzer adapted for high-pressure electrolytic systems has a cross-section so reduced in area as to be only sufficient to accommodate the gas bubbles passing through it when operating at high pressure. The vessel consists of a number of individual cells connected in series, the distance between elec-

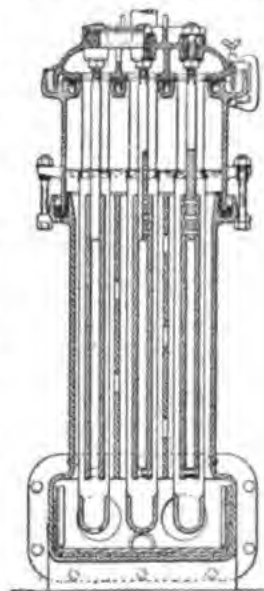


FIG. 253.

⁵² U. S. Pat. 1,219,843, Mar. 30, 1917.

⁵³ See also U. S. Pat. 1,221,206, Apr. 3, 1917.

⁵⁴ Brit. Pat. 318,734, Aug. 21, 1928, *Brit. Chem. Abst.*, 1930, 22B.

⁵⁵ Brit. Pat. 292,130, June 13, 1928, to Fauser, assignor to Montecatini Soc. Gen. per L'Ind. Min. ed Agric.; *Brit. Chem. Abst.*, 1929, 946B.

⁵⁶ Terano and Shimoyama, *Bull. Coll. Eng. Kyushu*, 1928, 3, 227; *Brit. Chem. Abst.*, 1929, 1013B.

⁵⁴ Brit. Pat. 101,598, May 11, 1916; *Chem. Abst.*, 1917, 122.

⁵⁵ *Chem. Met. Eng.*, 1928, 35, 421.

trodes of different polarity being greater at the bottom than at the top, while, in order to obtain smaller electrolyte-filled spaces, parts of the vessel are insulated against the electrolyte, so that the walls of the vessel can be used for conducting current. Partitions separating electrodes are made of asbestos cord, and yield to the variations of volume due to the different pressures of the gases.⁵⁶

6069B. Electrolysis of dilute sulphuric acid solution has been carried out between platinum electrodes, the acid being enclosed in a sealed glass tube with a space above the liquid in which the gases, hydrogen and oxygen, were collected, thereby increasing the pressure (to about 870 atmospheres) until it was sufficient to rupture the vessel. The results showed that the amount of current which could be passed increased with time, and therefore with gas pressure, until a maximum was reached.^{56a}

6069C. Fauser⁵⁷ considers the practical and economic difficulties involved in the electrolysis of water at high pressures to be virtually insurmountable. Theoretical considerations show that increase in the pressure is accompanied by increase in the amount by which the increment of the potential necessary to decompose water exceeds the ideal value of such increment. As regards the over-voltage, it is difficult to see how this can be diminished by effecting the electrolysis at a high pressure, since the gaseous layers surrounding the electrodes have then a higher density than at atmospheric pressure, and should thus offer increased resistance to the flow of the current. Further, any considerable influence of the pressure on the ohmic resistance of the electrolyte is excluded. Hence, of the various factors which intervene to modify the P.D. necessary for the electrolysis of water at high pressure, those increasing this P.D. prevail, so that there should be a global increment of the P.D. and of the energy required. It seems, therefore, that the saving in energy must be only apparent, and that the observed lowering of the E. M. F. must be counterbalanced by a smaller production of gas. Although the amounts of hydrogen and oxygen developed at the electrodes by the flow of a definite quantity of current are usually regarded as invariable, it is pointed out that the application of this law is limited in practice by secondary reactions between the elements separated. That nascent hydrogen and oxygen are able to react at the ordinary temperature is shown by the non-production of gas when water is electrolyzed by a symmetrical alternating current. These conclusions are supported by the experimental results obtained on electrolyzing water at pressures up to 1500 atmospheres, these showing diminution in the current gas-yield with increase of pressure; hence the accompanying depression of the P.D. is to be ascribed to depolarization phenomena.

6070. The Knowles Cell.⁵⁸ This cell is multipolar and although the floor space occupied is 60 per cent to 80 per cent more than that for a two electrode cell, the former cell is more cheaply constructed, and for large outputs of

⁵⁶ Brit. Pat. 268,426, Dec. 30, 1925, to Noeggerath; *Brit. Chem. Abst.*, 1927, 416B.

^{56a} Schnurmann, *Z. angew. Chem.*, 1929, 42, 949-952; *Brit. Chem. Abst.*, 1929, 945-6B.

⁵⁷ *Giorn. Chim. Ind. Appl.*, 1929, 11, 479-87; *Brit. Chem. Abst.*, 1930, 107B.

⁵⁸ The information in paragraphs 6070 to 6083 is derived from data kindly supplied by International Electrolytic Plant Co., Ltd.

hydrogen gas the lower cost of cell construction is said to counterbalance the increased cost for ground and buildings. The Knowles cell is shown partly in section in Fig. 254, from a study of which it will be seen that it consists of a tank containing the electrolyte, in which are suspended anodes and cathodes alternately, each covered by a collecting bell. The alternate plates in each cell are connected in parallel, while copper links at the ends of the cell couple up each set of electrodes in series with those of opposite polarity in the adjoining cells. The number of cells employed is controlled by the supply voltage, and

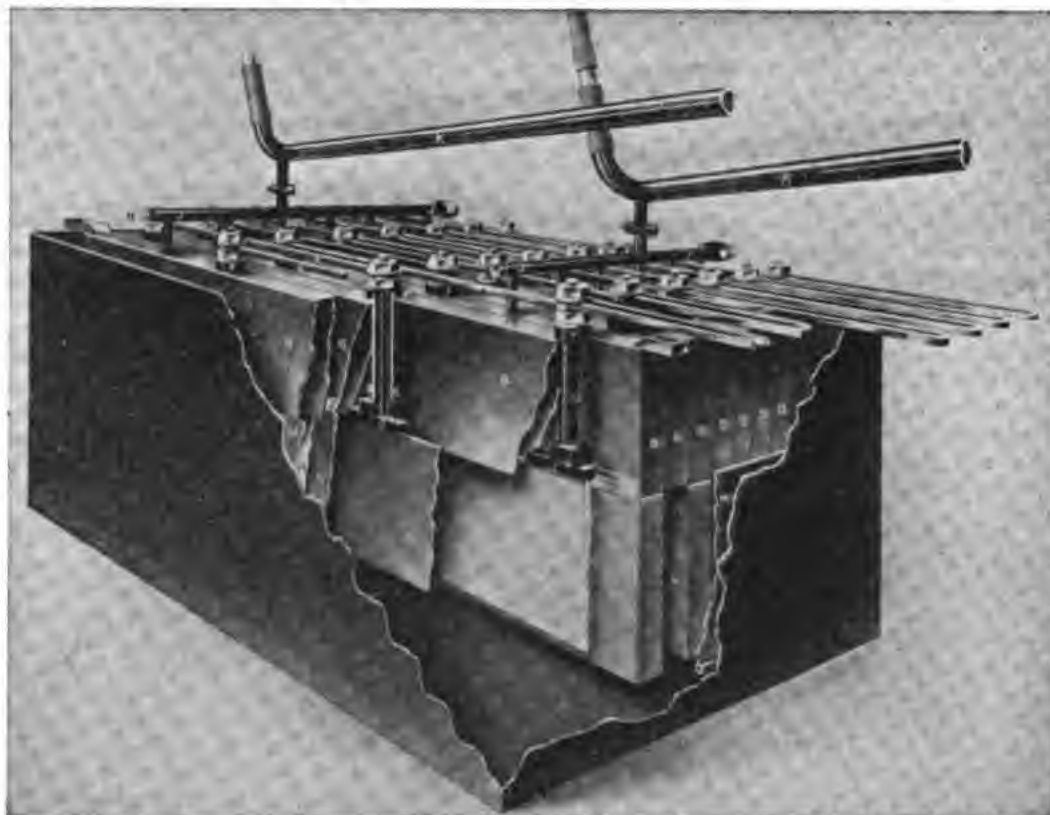


FIG. 254.

the number of bells per cell by the current necessary with this voltage to produce the output of gas required.

6071. The arrangement, in fact, is that used for years past in the copper refining industry and known as the multiple system of cell working, for while all the electrodes of one polarity in one cell are connected in parallel, the cells themselves are connected in series. The similarity to the copper refining tank system, however, ends here, for the upper part of each electrode in the Knowles cell is covered by a sheet iron collecting hood for retaining the gas liberated by the electrolysis, and the lower part is surrounded by an asbestos petticoat or diaphragm, which is designed to prevent all danger of the gases becoming mixed

before they leave. Each electrode and collecting bell, therefore, is a complete unit in itself, but all the bells in one cell are connected rigidly together and may be lifted from the tank complete with their connections, in one operation, by a suitable overhead crane.

6072. The current is led to the electrodes by staggered bolts *C* with terminals on the tops of the bells. The oxygen and hydrogen are carried off from the bells by the two pipes *JJ* running across the top of the cells, which in turn connect with common offtake pipes for each bank of cells. The gas evolved by the cells carries with it a certain amount of electrolyte in the form of a fine spray, which is collected in offtake pipes specially formed to assist in returning liquid to the cells. Each bank of cells is supplied with distilled water by gravity from a feed tank placed at the end of the row. The inlet to this feed tank is controlled by a ball valve, so that the level of the electrolyte remains constant and is independent of the quantity of gas being evolved. The electrolyte consists of a 15 per cent solution of the best quality caustic soda in pure distilled water, and once a solution of the right strength is made up the only addition required is distilled water. It is, however, of the utmost importance that this water shall be absolutely pure, for the durability of the cells is very largely dependent upon its purity.

6073. Figure 254 shows also that the bolts *CC*, which conduct the current to the electrodes, are insulated from the sealing tubes *DD* by ebonite sleeves *EE* and top insulating rings *FF*. Copper bars connect the two bolts in one electrode, in order to ensure equal current distribution, and copper cross strips are employed for placing the anodes and cathodes in parallel connection with the main current leads.

6074. A large factor in the success of the Knowles cell is its simplicity of construction. All the bells are welded together to form one solid block, and by simply disconnecting the offtake pipes and electrical connections they may be lifted from the tank with the electrodes for inspection, adjustment or overhauling. It is, however, seldom necessary to cut out a cell for this purpose, provided that the plant is properly handled and nothing but pure distilled water is added to the electrolyte. By simply unscrewing the nuts forming the terminals of the electrode bolts the electrodes and insulators are readily accessible for examination or replacement.

6075. Some of the advantages claimed for the Knowles cell construction are: (1) The electrodes are each supported by two or more leads, and these leads are staggered so that a very even distribution of current takes place. (2) These leads hang loosely down a tube open at the bottom and welded to the collecting bell at the top, and this tube forms a seal in the electrolyte, making it impossible to run the level of the electrolyte so low that any leakage of gas can take place around the bottom of the collecting bells. (3) These open tubes therefore allow the gas to escape around the leads long before a danger point can be reached, and this effect is further secured by an extra tube, quite empty, attached to each set of cathode bells in each cell. (4) The electrodes are kept so short that the cells will work satisfactorily without diaphragms, these being added only to make the separation of the gases more perfect.

6076. As regards industrial developments, it is learned from a reliable source that the cell is being operated in this country and abroad upon a scale which is producing in the aggregate over 100,000,000 cu. ft. of hydrogen per year, and that many of these plants have been in use for several years at a high efficiency, with low charges for repairs and depreciation.

6077. The 5000 amperes type of cell produces 80 cu. ft. of hydrogen and 40 cu. ft. of oxygen per clock-hour. The best working conditions as regards economy can only be ascertained by studying the local conditions.

6078. Detailed Description. A partly sectioned view of a 14-bell cell is shown in Fig. 254, in which the various parts are clearly visible. The block of bells forming the gas-collecting chambers is supported by lugs resting on the edge of the tank containing the electrolyte so that the whole of the internal parts of the cell may be removed as one unit by simply disconnecting the copper connections and gas offtake pipes. The electrodes *AA*, alternately positive and negative, are suspended by bolts *CC* from the bells *BB*. The bolts *CC* pass through steel tubes *DD* welded into the top of the bells and are insulated therefrom by insulating tubes *EE*. The end of each electrode bolt carries two nuts insulated from the steel tubes by caps *FF* on which the bottom nuts rest and carry the weight of the electrodes. Current is conveyed to the electrodes by copper connections *GG* clamped between these nuts. Gas offtake pipes *JJ*, one for each gas, collect the gas from alternate bells and these in turn are coupled to specially shaped pipes *KK*, one each for oxygen and hydrogen, running along the row of

cells. The electrodes are separated by asbestos diaphragms *LL* open at their lower ends. A skirting *MM* surrounds the entire block of bells and forms a stand on which it rests when removed from the tank.

6079. Knowles Compact Column Cell. A drawback to the use of electrolytic cells for the production of hydrogen in large volumes has always been the

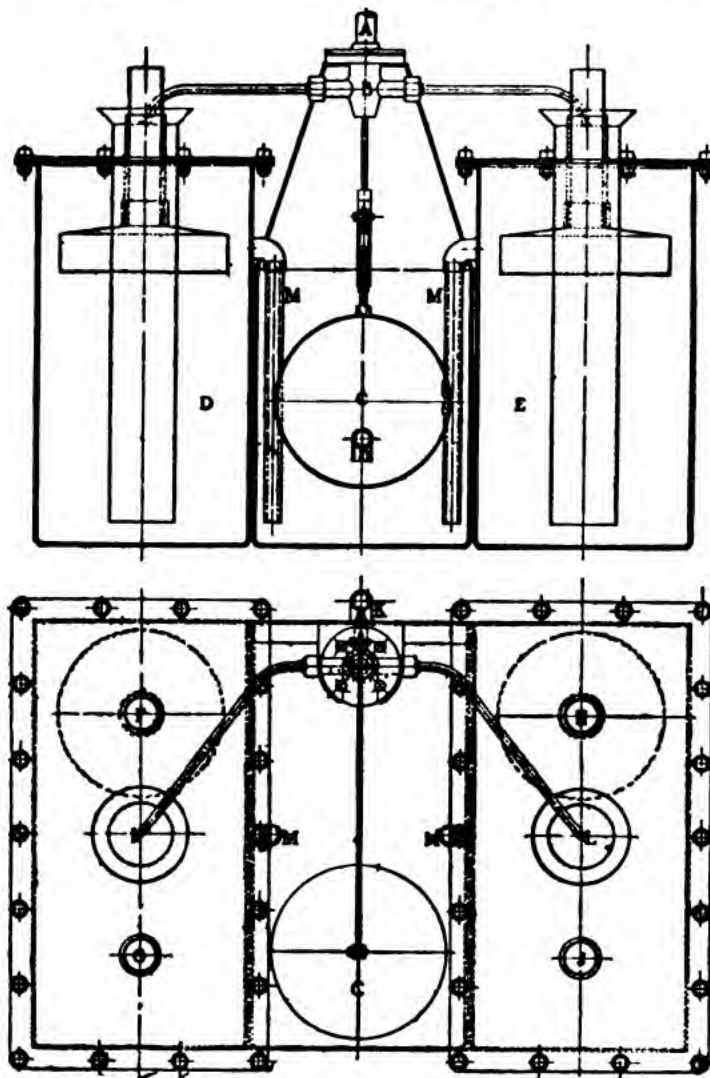


FIG. 255.—DIAGRAMMATIC DRAWING OF AUTOMATIC FEED USED IN THE KNOWLES EQUIPMENT, SHOWING THE MANNER IN WHICH THE GASES ARE WASHED.

Distilled water which is to be used to supply the cells is employed to wash the caustic alkali spray from the gases. By this procedure the loss of alkali becomes negligible. The parts of this automatic feed are designated as follows: *A*. Distilled water inlet. *B*. Piston valve. *C*. Ball float. *D*. Oxygen washing tank. *E*. Hydrogen washing tank. *F*. Oxygen inlet. *G*. Oxygen outlet. *H*. Hydrogen inlet. *J*. Hydrogen outlet. *K*. Distilled water outlet to cells. *L*. Water inlet to washing tank. *M*. Overflow pipe to center tank.

great floor space required. With the recent rapid developments in the synthetic ammonia industry and other similar processes, the question of floor space has

been brought into special prominence, not only on account of the exceptionally large plant required but also because such plants have usually to be installed where much expensive excavating work is necessary to provide a level area for

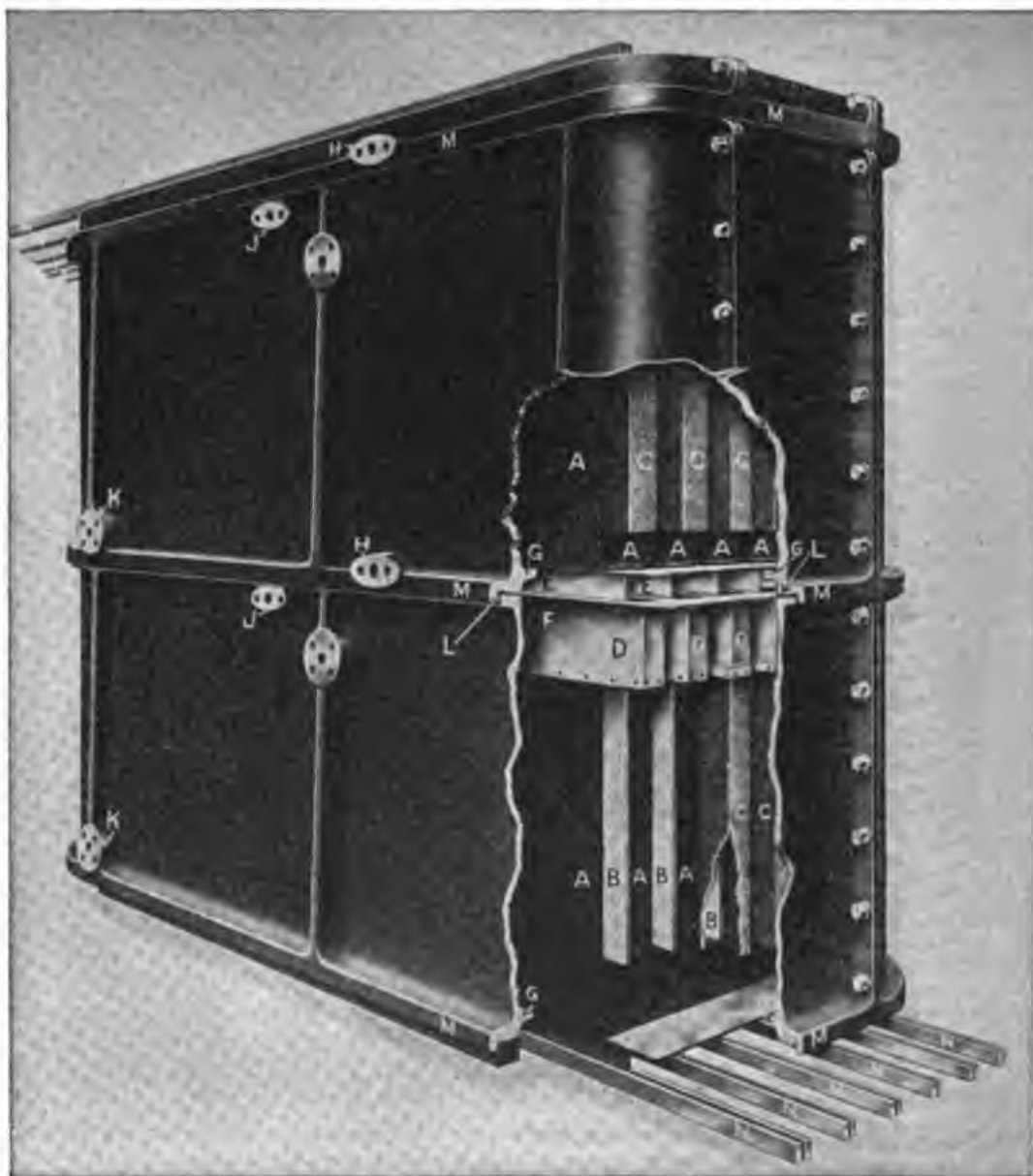


FIG. 256.

the cell room. This is naturally so, as in nearly every case the source of power is hydro-electric and the site for the works is consequently nearly always in mountainous districts.

6080. Hitherto, floor area has been reduced by increasing the depth of the electrodes and running them at very high current densities, which seriously

reduces the life of the cell and also increases its internal resistance, resulting eventually in a serious loss of efficiency. Even cells with exceptionally deep electrodes run at very high current densities do not enable the floor area to be very greatly reduced and anything saved on the initial cost of the buildings may be soon expended on the greater cost of upkeep involved.

6081. The Knowles Column Type plant, on the other hand, has electrodes of only moderate depth running at low current density and yet it is claimed that it occupies much less floor area than is usually required.

6082. It will be seen from the sectioned photograph (Fig. 256) that the general design of each cell is similar in some respects to a bell type cell and does not

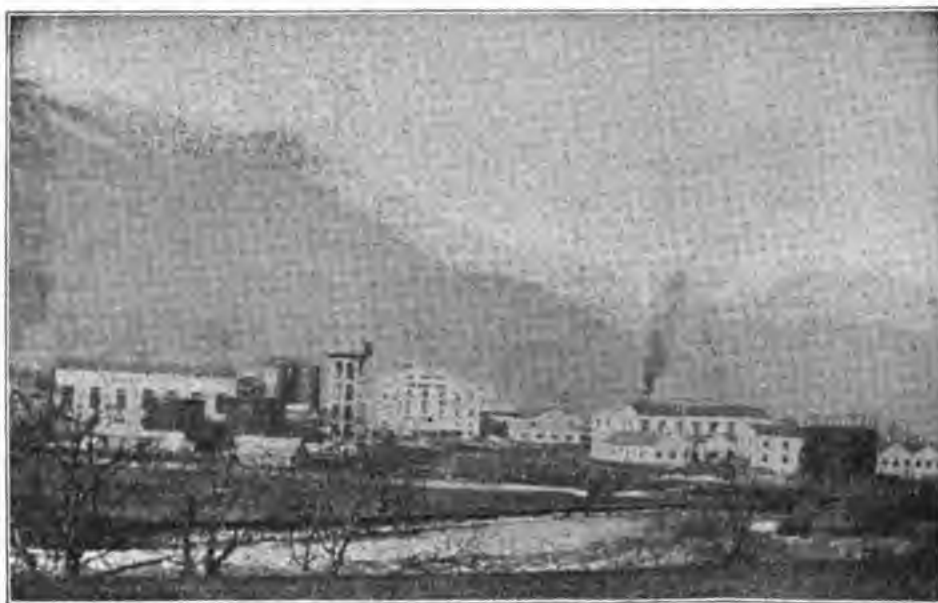


FIG. 257.—SOCIÉTÉ DES ENGRAIS AZOTES ET COMPOSÉS USINE SOULOM. PIERREFITTE-NESTALAS H. P., FRANCE.

In the foreground on the right is the gasholder for receiving the hydrogen produced by the Knowles electrolytic plant of 800 cells which is in the series of buildings behind the gasholder. The tall building in the center contains six converters of 3750 KW. each, supplying the electricity used by the plant.

depart from principles acknowledged to be best in electrolytic cell design. The superimposed arrangement adopted is, however, novel and enables a plant of large capacity to be installed on an exceptionally small area. For the sake of clearness, the illustration shows only two cells, but in practice the cells can be erected ten high. The current passes directly from each cell to the cell above, without any external connections, the polarity being reversed as it passes from one cell to the next, and the only electrical connections required are to the bottom of the lowermost cell and to the cover of the upper cell of each column. Upstanding electrodes on the base of one cell alternate with electrodes hanging from the base of the cell above, and form the anodes and cathodes respectively of each cell unit. Asbestos diaphragms suspended from the dividing or bell plate

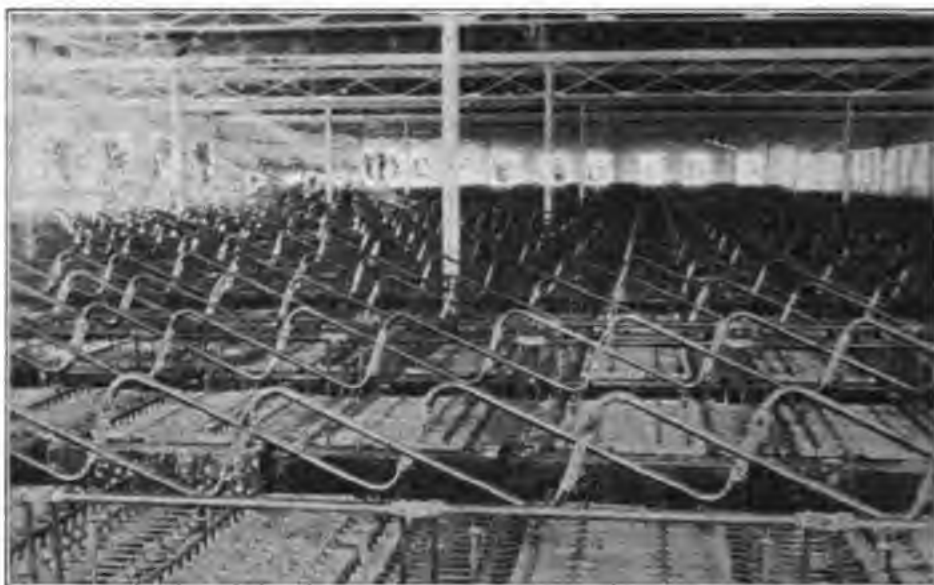


FIG. 258.—KNOWLES PLANT AT PIERREFITTE, FRANCE.

Comprising 800 cells absorbing 8600 amperes, and producing 3140 cubic meters of hydrogen per hour. General view across cell room.



FIG. 259.—KNOWLES PLANT AT PIERREFITTE, FRANCE.

Automatic water feed and gas washing tanks on the left, ends of rows of cells with bush-bars on the right, and gas pipes to washer tanks over gangway.

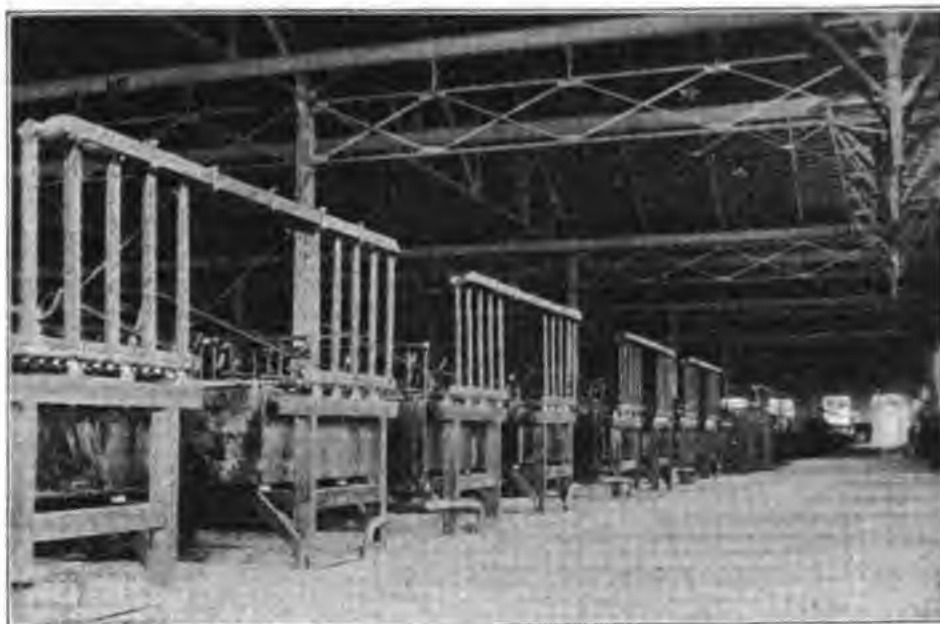


FIG. 260.—KNOWLES PLANT AT PIERREFITTE, FRANCE.

Ends of rows of cells farthest from washer tanks.



FIG. 261.—KNOWLES PLANT AT PIERREFITTE, FRANCE.

Ends of rows of cells showing on the right copper strip connections to end cell in one battery from rotary converters.

surround the hanging electrodes and prevent the gases which collect in the spaces from mixing. The containing tank, the inner surface of which carries an electrode, is built up of four iron castings bolted together and is of a specially rigid construction to carry the weight of the cells above. All the tanks in any particular plant are identical and interchangeable, so that any tank may be used for the bottom cell without risk of failure from the weight above. The base of the tank to which the electrodes are fixed rests on a projection and is bolted to it to form an electrolyte-tight and gas-tight joint. Suitable electrolyte separators and vertical gas offtake pipes are provided and also a makeup water inlet. The tanks of adjacent cells are insulated from one another by special jointing rings which also form a gas-tight joint and insulate the bell plate from both the tank above and below it. There is no possibility of a short circuit occurring

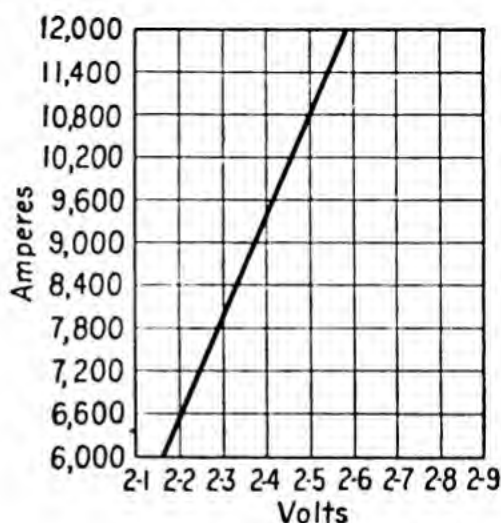


FIG. 262.

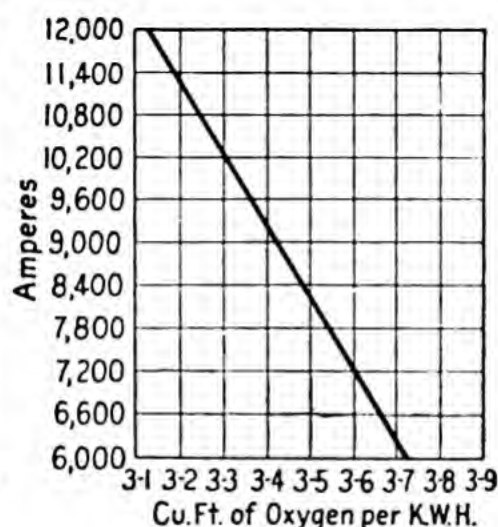


FIG. 263.

between adjacent tanks as any electrolyte which may drip from a faulty pipe connection on the cell above falls clear from the projecting flange when it reaches the bottom of the tank. Due to the weight of the cells and electrolyte, no holding down bolts are necessary to make the joint between the tanks gas-tight, and erection or dismantling is done by lifting the whole cell complete with electrodes.

6083. Performance. Normally the cells run at 2.25 volts per cell, but are quite capable of running at any voltage up to 2.5, at which figure the gas production is 50 per cent above normal. The voltage may also be reduced to 2 volts per cell, representing a decrease in current consumption of 50 per cent below normal giving a corresponding decrease in the gas output, but with increased efficiency. This flexibility in operation is of great importance when the cells are to be used in connection with "off-peak" power schemes where the power available varies greatly during the twenty-four hours of the day. Figure 262 shows the relation between current and voltage in a cell designed to operate normally at 7200

amperes, but the same curve applies equally to cells of other capacities by merely increasing or decreasing the current scale in proportion. In a similar way, curve, Fig. 263, applies to cells of any output.

6084. Porous Diaphragm for Electrolytic Cell. Jaubert⁴⁰ forms a diaphragm suitable for use in electrolysis of alkaline solutions which comprises material such as perforated sheet metal, wire gauze or asbestos cloth carrying a coating and filler of a hydrogel of an organic or inorganic colloid such as may be formed by dipping the material in a solution of magnesium chloride or sulphate and then in a sodium silicate solution. The colloid may also be deposited on the diaphragm by a preliminary electrolytic treatment. When potassium or sodium carbonate is used for the electrolyte, a hydrogel of magnesium hydrocarbonate may be used. Among the other colloids which may be employed are: iron silicate, kaolin, ferric hydroxide, natural or artificial yellow ocher, limonites, clays, magnesium or aluminum phosphates, graphite, wood charcoal, rubber, hydrates of alkaline earth or rare earth metals, and copper, nickel or other metal in flocculent form. When not in use the diaphragm may be dipped in a 50 per cent glycerol solution to prevent it from drying.

6085. Casale⁴¹ forms the electrodes of wire mesh or perforated metal. Scott⁴¹ uses permeable material permitting circulation of the electrolyte to the rear of the adjacent faces.

6085A. Methods of production and fields of utilization of oxygen and hydrogen are reviewed by Dobson and Barnes, *Amer. Electrochem. Soc.*, Sept., 1929, advance copy; *Brit. Chem. Abst.*, 1929, 938B. Further possible outlets for these gases are considered and the prospects of the electrolytic process for producing them discussed.

AUTOMATIC CONTROL

6086. The control of the electric current employed in electrolysis of water to produce oxygen and hydrogen is of importance. Precautions must be taken against the discharge of current in a reverse direction from the electrolyzers through the generator. This condition, if allowed to develop, may result in reversal of the source of energy and consequent reverse functioning of the electrolyzers with the attendant mixing of gases. There is also to be observed the prevention of improper connection of terminals at the bank of electrolyzers during or after overhauling or for other reasons. The Davis-Bournonville Company developed an electrolyzer control designed to prevent reversal of current direction through cutting off the source of supply automatically.

6087. Figure 264 shows, in a general manner, the electrical connections and methods of control. Figure 265 shows the equipment assembled on a panel. The necessary indicating volt ammeters, *C* and *D*, respectively, are mounted on each panel of this design; also, the necessary instruments for the automatic control of the electrolyzing circuit. The generator *A* is the source of electrical energy for the electrolyzers and its field regulator *B* is also mounted upon this panel.⁴²

6088. The electrolyzer current proper, *H*, is controlled solely through the magnetic contactor *F*, the magnetic coil of which is wound for operation across the independent supply mains *G*. This independent supply main can be either alternating or direct current of any voltage. This independent circuit *G* is controlled at three separate and distinct points, as follows:

- 1st—Potential Relay *E*,
- 2d—Contactor Pilot Switch, hand reset, *J*,
- 3d—Overload Relay, hand reset, *M*.

⁴⁰ Brit. Pat. 281,674, Dec. 1, 1926; *Chem. Abst.*, 1928, 22, 3591.

⁴¹ Brit. Pat. 268,998, June 1, 1926.

⁴² Brit. Pat. 210,102, July 25, 1922.

⁴³ U. S. Pat. 1,201,526, Oct. 17, 1916, to Swartley and Larsen.

6089. The potential relay *E* is set to lift at a predetermined operating or charging voltage, thereby completing the electric circuit, which will throw into play the magnetic contactor *F*. This means that with the contactor pilot switch *J*, held closed and the overload relay closed, not until the generator will have reached the predetermined charging voltage will the potential relay close the independent circuit from the power lines. It will be noted that it is impossible to pass electrical energy through the electrolyzers until the generator attains the charging voltage.

6090. If, for any reason, during operation the generator voltage should drop below the charging voltage, the potential relay *E* will automatically drop out, opening the magnetic contactor, thereby breaking the electrolyzing circuit. This method of control entirely prevents the electrolyzers from discharging to the generator *A*, with the consequent possibility of polarity changes, if, through error or deliberately reversing electrical connections, the direction of flow of electrical current is changed. The smallest fraction of a reversed current through the shunt *N* brings the polarized relay into play, breaking the contact in the contactor switch *J* which, in turn, breaks the current through the coil of the potential relay *E*, thereby

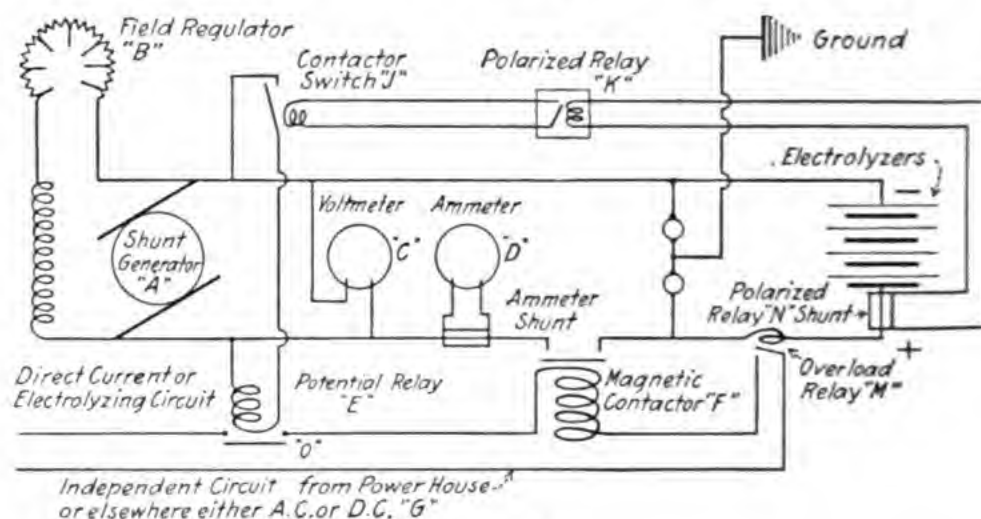


FIG. 264.

releasing the connection *O* and breaking the circuit *G*, which drops out the magnetic contactor *F* which interrupts the main electric circuit to the electrolyzers. This makes it absolutely impossible to operate on a reverse polarity.

6091. The overload relay is manually operated and is calibrated slightly in excess of the normal operating amperage. In case of opening of the circuit, due to overload, it will be noted that the overload relay *M* will have to be reset by hand before the electrolyzing circuit can again be established.

6092. Under normal operating conditions the ground detector lights *Q* will glow slightly but, in case of a ground on one or both legs of the electrolyzing circuit, either or both of the lamps will glow brilliantly, showing the ground to exist.

6093. Hausmeister⁶³ secures the purity of oxygen and hydrogen or other gases generated from an electrolyte in a closed container by maintaining a constant pressure in the container thereby preventing the release of a mixture of gases due to variations in pressure.

6094. According to Seville,⁶⁴ hydrogen and oxygen are generated electrolytically, then cooled as they pass from the generator into separate containers, the condensed moisture being led back into the generator. A diaphragm is so arranged, containing chambers through which the gases pass on their way to their respective containers, that a predetermined difference of pressure on one side of the system causes the diaphragm to close the gas entrance to

⁶³ U. S. Pat. 1,581,944, Apr. 20, 1926.

⁶⁴ U. S. Pat. 1,230,803, June 19, 1917.

the opposite container, until a balancing pressure has again been raised on that side. By means of a body of water the gases are automatically compressed to a pressure higher than that originally generated. Sebille⁶⁶ also describes a system of gas storage chambers having automatically-controlled valves regulating the flow of gases.

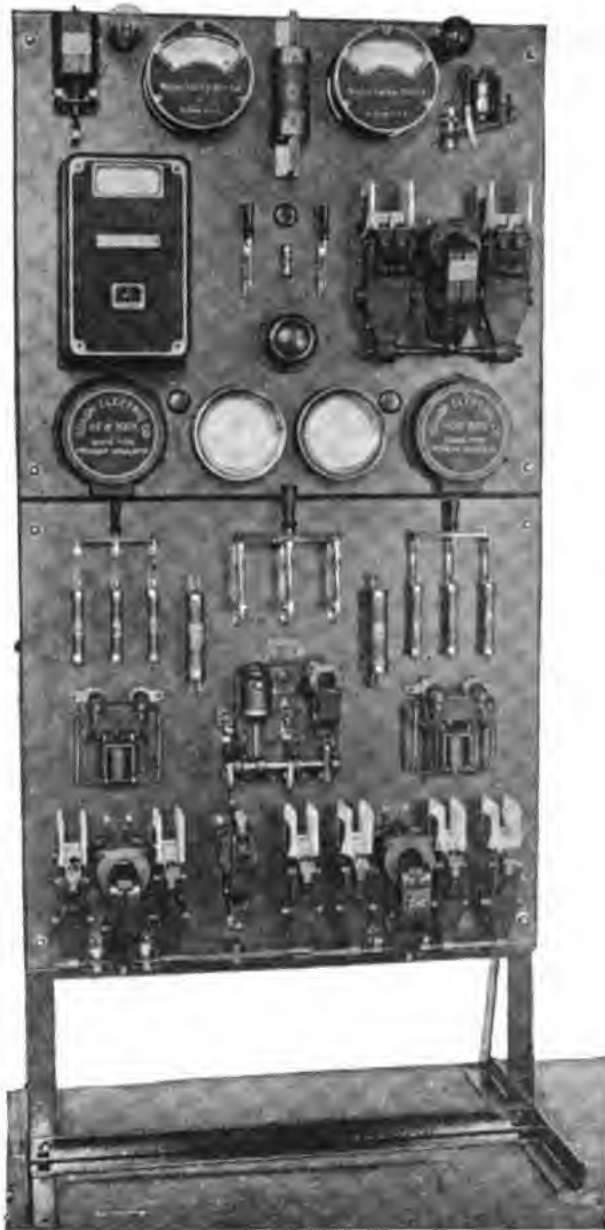


FIG. 265.

6095. Separation of Oxygen and Hydrogen.⁶⁶ When oxygen and hydrogen have been electrolytically generated without separation the mixture is collected in a confined space under pressure, dried by cooling, and cooled in the condensing apparatus by liquid nitrogen to the

⁶⁶ U. S. Pat. 1,222,809, Apr. 17, 1917.

⁶⁶ The Consortium für elektro-chem. Ind., Ger Pat. 414,187, Feb. 9, 1924.

liquefying point of the oxygen. The cooling effect is produced by vaporizing liquid nitrogen under reduced pressure, for example by means of the separated hydrogen. The collecting apparatus for the electrolytic gas is arranged so that an accidental explosion will not produce harmful effects.

6096. Water Decomposition in the Arc. Dansette ⁶⁷ has devised an arrangement for feeding water vapor into the zone of an electric arc produced in a gas-tight electric furnace, by passing water through the lower, vertical, carbon tube, which constitutes one of the electrodes. The furnace communicates by means of a valve with a reservoir, into which the hydrogen and oxygen produced by dissociation pass. The oxygen may either be absorbed by a suitable reagent, or the two gases separated by diffusion through a porous earthenware vessel.

⁶⁷ French Pat. 391,793, Sept. 6, 1907.

CHAPTER LXI

MISCELLANEOUS PROCESSES FOR MAKING HYDROGEN

6100. The older processes that we shall consider in this chapter have but little industrial application. Most of them, however, have been of importance in aeronautics and as occasional sources of hydrogen. Among the newer methods there are some which may be developed industrially.

6101. Much attention has been given to the production of hydrogen by chemicals, which, when added to water or hydrated substances, liberate hydrogen freely, thus enabling the generation of hydrogen at any point without the necessity of setting up elaborate apparatus.

6102. Powdered aluminum or silicon and alkali, "activated" aluminum and water, ferrosilicon and calcium hydrate, calcium hydride and the like have been proposed under various names such as hydrone, hydrogenite, the Hydrik process, etc. Bergius has brought out a process involving the treatment of carbon or iron with water in a liquid condition under very high pressures.

6103. Foersterling and Philipp¹ generate hydrogen by causing water, in a finely divided state, to react successively with relatively small masses of sodium, separated from each other, in the same containing vessel, in such a way that the supply of hydrogen is continuous, and at a rate that substantially prevents a solution being formed. They also propose silicides for the generation of hydrogen. An intimate mixture of equal parts by weight of sodium and aluminum silicide ("sical") is prepared by heating the two substances in a kneading machine until all the sodium is molten; the kneading appliance is then put into operation and kept continuously rotating while the mixture cools down, after which the latter is transferred to a press and briquetted. One kilo of the mixture, when acted on by water, generates about 700 liters of hydrogen, the reaction being represented by the equation,



6104. Brindley² treats an alkali or alkaline-earth metal, for example sodium, in a finely divided state, with a crude hydrocarbon oil or similar substance, which will temporarily prevent oxidation of the metal, and with an inert substance such as infusorial earth, and the mixture is compressed into tablets or briquettes, which when brought into contact with water will generate hydrogen. In order to increase the yield of hydrogen, a metal (aluminum, silicon) which forms a hydroxide, the hydrogen of which can be replaced by an alkali or alkaline-earth metal, is also incorporated in the mixture.

6105. Philipp³ generates hydrogen by the action of water on a mixture of metallic sodium and aluminum silicide. The action of water on this mixture does not proceed to completion, and the method consists in first treating the mixture with water, and then passing the hot hydrogen and steam through a similar mixture which has previously been partially decomposed by treatment with water.

¹ U. S. Pat. 883,531, Mar. 31, 1908.

² U. S. Pat. 909,536, Sept. 14, 1909.

³ U. S. Pat. 1,041,865, Oct. 22, 1912.

6106. A variant on zinc solution is afforded by a unique device described by Gardiner and Hulett.⁴ A sodium hydroxide solution, containing some barium hydroxide, is electrolyzed between an amalgamated zinc anode and a cathode of platinum-black or of nickel, without the aid of an external current. The generator operates at full capacity on short circuiting the electrodes. The gas supply is controlled by interposing a variable resistance. No oxygen is produced and, in order to prevent the formation of a dead air space, the alkali solution is saturated with hydrogen before setting up the apparatus.

6107. A number of processes depend on the reaction between silicon in some form (usually ferrosilicon) and caustic soda.

6108. The Siemens & Schuckert Company worked out a process for the production of hydrogen from the reaction between silicon and caustic soda solution. At first steam was employed, but later the heat set free during the reaction was found sufficient to maintain the proper conditions. The evolution of hydrogen gas takes place when a 25 per cent solution of caustic soda acts on silicon introduced in small quantities. The capacity of a transportable plant is 60 to 120 cu. m. per hour, while stationary plants are built for capacities up to 300 cu. m. per hour. The process is a neat one, but the cost of production of hydrogen is high.⁵

6109. A somewhat similar system is used in France under the name of the Silicol process. Ferrosilicon or other silicon alloy is treated with freshly prepared 35 to 40 per cent caustic soda solution. The heat of solution of the alkali raises the temperature to 60° to 80° and enables the reaction to progress rapidly. Hydrogen by this method likewise is costly.⁶

6109A. In another process of this type,^{6a} silicon or ferro-silicon is introduced progressively and in adjustable amount into caustic alkali solution in a closed vessel under pressure by means of an adjustable distributor.

6110. Jaubert⁷ uses a strong solution of a caustic alkali, or a solution of sodium or potassium sulphate containing such, which is made to act upon a compound or alloy of silicon (preferably ferrosilicon, manganosilicon or silicospiegel) in such a way that the heat produced in preparing the alkali solution is utilized in effecting the reaction, no external heat being required. The reaction takes place in a generating vessel, fitted with a stirring device and surmounted by a feeding hopper containing the powdered alloy; this vessel communicates both with an arrangement for washing and cooling the gas and with another vessel, also provided with a stirrer, in which the solution of caustic alkali is prepared (e.g., by dissolving 1 part by weight of sodium hydroxide in 1½ to 2 parts of water). The water which has served to cool the gas in the condenser passes either to the generator or to the dissolving vessel. A strong solution of alkali being used, an acid silicate is obtained; moreover, non-caustic residues, suitable for use in dyeing and bleaching, are obtained.

6111. The preparation of hydrogen under pressure by the wet method is detailed by Jaubert⁸ as follows: The reaction by which the hydrogen is produced is carried out under a pressure above the vapor pressure of water at the temperature in question, the larger part of the heat produced is localized and stored in the reacting liquid, and by preventing the vaporization of this liquid, dry hydrogen is obtained, the speed of manufacture is increased, and the amount of liquid necessary for the reaction diminished. The pressure is produced automatically by working with an autoclave generator, in which the hydrogen produced is allowed to accumulate. The generator is a revolving cylinder, provided with an autoclave cover, a charging chamber which penetrates some distance into the interior of the cylinder and a blow-off cock, so that complete mixing of the reagents can be prevented before the reaction is started and to allow the hydrogen formed to be drawn off.

6112. To obtain a rapid and constant evolution of hydrogen by the interaction of silicon,

⁴ *Trans. Amer. Electrochem. Soc.*, 1928, **54**, cited (from an advance copy) in *Rep. Progress Appl. Chem.*, 1928, 331.

⁵ *Met. and Chem. Eng.*, 1911, 157.

⁶ See *Zeitsch. f. angew. Chem.*, 1912, 2405.

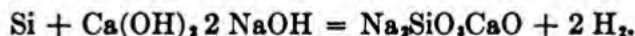
^{6a} *Brit. Pat.* 294,150, July 17, 1928, to Oxyhydrique Franc.; *Brit. Chem. Abst.*, 1929, 814B. See also U. S. Pat. 1,752,187, March 25, 1930; *Brit. Chem. Abst.*, 1930, 419B.

⁷ *French Pat.* 430,302, Aug. 6, 1910.

⁸ *French Pat.* 433,400, Oct. 25, 1910.

aluminum or alloys containing the same, with an alkali hydroxide, Jaubert⁹ prepares an emulsion of a concentrated solution of the latter with a non-saponifiable oil or grease, such as paraffin, which mixture is heated to 100° C., with the elements or alloys named, in the form of fine powder, water being added as fast as it is decomposed, and the frothy mass being kept constantly agitated.¹⁰

6113. The Hydrogenit process of Jaubert¹¹ involves mixing finely powdered ferrosilicon with soda-lime to produce a grayish granular mass which easily ignites and burns readily even with exclusion of air, the reaction being



From 3 kilos of the mixture, which, by the way, is stable at ordinary temperature, about 1 cu. m. of very pure hydrogen is obtained. The mixture is pressed to blocks and is shipped in metal containers holding 25 to 50 kilos, affording 8 to 16 cu. m. hydrogen in about a ten-minute period. The mixture is kindled by a small amount of ignition powder or quick-match. Equipments for furnishing 150 cu. m. hydrogen per hour have been made.

6114. A case of Hydrogenit is placed in each generator. The cover of the generator is put on and clamped in place and the mixture lighted through a closable opening in the cover. The generators are equipped with water jackets and the steam produced by the heat of the reaction is, towards the end of the run, turned into the generator, giving a larger yield of hydrogen. The gas is washed and dried. The cost of hydrogen made from Hydrogenit is high.

6115. Jaubert¹² has described the following modification of the above. Metals such as aluminum or zinc, or their alloys, or metalloids such as silicon or carbon, or their compounds, e.g., ferrosilicon, when mixed with alkali or alkaline-earth hydroxides in the form of dry powders, yield mixtures quite stable at ordinary temperatures. If, however, reaction be induced by local application of heat, hydrogen is evolved and sufficient heat is developed to cause the propagation of the reaction throughout the mass. A suitable apparatus consists of a tube closed at one end by a screw cap and having near this end an opening (with a screw cap) through which a quick-match or piece of hot iron may be introduced to induce the commencement of the reaction. The other end of the tube is formed by a perforated plate, through which the hydrogen evolved passes into a chamber packed with filtering material, and thence into an annular space formed between the tube and a jacket extending nearly the whole length of the latter. The hydrogen accumulates in this annular space under pressure, and is withdrawn as required through a suitable outlet.

6116. Ferrosilicon containing 75 per cent of silicon, when heated to a very high temperature is capable of decomposing steam with sufficient evolution of heat to carry on the reaction.



The reaction may be regulated by the addition of lime, which has the further advantage of forming an easily workable slag. The apparatus comprises a refractory chamber surrounded by a steam coil, the delivery end of which terminates in a series of injectors, which admit steam into the chamber; a feeding hopper is provided at the top of the chamber and a door for the withdrawal of the slag at the bottom.¹³

6117. By the addition of lime, or calcium compounds that form lime, according to¹⁴ Consortium für Elektro-chem. Ind. Ges. m. b. H., nearly the full theoretical quantity of hydrogen

⁹ French Pat. 454,616, Apr. 30, 1912.

¹⁰ See also U. S. Pats. to Jaubert: 943,022, Dec. 14, 1909; 1,029,064, June 11, 1912; 1,037,919, Sept. 10, 1912; 1,040,204, Oct. 1, 1912. For a ferrosilicon method, available in the field in the absence of a supply of water, see Lefebvre, *Chimie et Industrie*, 1928, **30**, 231; *Chem. Abstr.*, 1928, **22**, 4732.

¹¹ Ger. Pat. 236,974.

¹² French Pat. 422,296, Jan. 14, 1910.

¹³ Jaubert, French Pat. 438,021, Mar. 4, 1911.

¹⁴ Brit. Pat. 21,032, Sept. 14, 1909.

is rapidly liberated on heating silicon in an aqueous solution of caustic alkali. The process may be carried out in an iron generator fitted with stirrers. The temperature necessary for the generation of hydrogen from silicon and caustic alkali solutions may be obtained by the solution of the powdered alkali or alkali oxides in water, or by the heat produced in the chemical reaction between aluminum or aluminum alloys and the alkali.¹⁵

6118. An alkali or alkaline-earth hydroxide, or a mixture of the two, is mixed with charcoal and a finely divided metal or mixture of metals, and the whole is heated in a hermetically sealed vessel, with the exclusion of air, and under diminished pressure. Under the action of the metal, according to Hlavati,¹⁶ the hydroxide is converted into oxide, and hydrogen and carbon monoxide are formed.

6119. Hydrogen is produced in the dry process of Jaubert¹⁷ by ignition and autocombustion, in a closed generator, of a mixture consisting of an excess of a combustible substance (metal, metalloid or alloy), capable of decomposing steam at a high temperature, an oxidizer or other substance to maintain the combustion, and a substance evolving steam on heating (which is omitted, partially or wholly, if steam be introduced from an external source).

6120. Suitable mixtures, which may be packed in metal cartridges, to be opened and placed directly in the generator, are the following: (a) Powdered iron 20 kilos, slaked lime 10, potassium perchlorate 6, (b) ferrosilicon, with 75 per cent of silicon, 20, litharge 10, soda-lime, containing two-thirds of sodium hydroxide 60; (c) ferrosilicon 20, powdered iron 5, wheat flour 3, lime 5, and potassium chlorate 3. If the ingredient evolving steam be omitted, the generator may be surrounded by a water jacket, the two vessels being connected so that the necessary steam is supplied from the latter by the heat of the reaction; a pipe from the generator conveys the gas either to the exterior or through a purifying and drying apparatus, to be utilized. The generator described is closed by a heavy lid which, for safety, is held in position by its own weight.

6121. Baillio¹⁸ produces hydrogen and sodium silicate by the following method. An excess of silicon is repeatedly acted on with 10 per cent caustic soda solution, in a closed vessel and the hydrogen and sodium silicate solution produced by each treatment are removed before adding fresh caustic soda solution.

6122. In Teed's process for the manufacture of hydrogen from ferrosilicon and caustic soda the residual sludge is continuously discharged into a trap adapted to be raised or tilted to prevent the ingress of air into the generator, while allowing the entire plant to be purged periodically to carry away any air which may leak into the system at other places. Should the pressure in the generator rise above a predetermined limit, the excess gas bubbles through a hydraulic seal into the atmosphere. The gas and steam from the generator pass through a condenser and the condensed water is returned wholly or in part to the generator to keep the strength of the solution more or less constant.¹⁹

6123. Brindley and Bennie²⁰ use a mixture consisting of finely divided aluminum and molten sodium hydroxide, the proportion of the latter being between 1 and 3 mols. to 1 mol. of aluminum. Silicon and zinc may also be added.

6124. By the Hydrik process aluminum powder is acted on by caustic soda giving hydrogen and sodium aluminate, according to the equation,

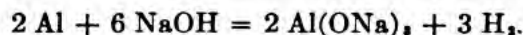


Fig. 266 shows a gas generator for the Hydrik process with an hourly capacity of 10 cu. m.

6125. Mauricheau-Beaupre²¹ adds to fine aluminum filings a small proportion of mercuric chloride and potassium cyanide, which causes a slight rise of temperature and produces a coarse powder, quite stable if kept from mois-

¹⁵ Brit. Pat. 11,640, May 13, 1911.

¹⁶ Ger. Pat. 250,128, Feb. 25, 1911.

¹⁷ French Pat. 427,191, May 21, 1910.

¹⁸ U. S. Pat. 1,178,205; *Chem. Abst.*, 1916, 1582; *J.S.C.I.*, 1916, 633.

¹⁹ Brit. Pat. 250,700, Jan. 27, 1925, to Airship Guarantee Co., Ltd., and Teed.

²⁰ U. S. Pat. 943,036, Sept. 14, 1909.

²¹ *Compt. rend.*, 1908, 147, 310.

ture. This powder is treated with water (about 1 liter to a kilo) and the rise of temperature which occurs as the hydrogen is evolved is watched, and regulated if necessary by the addition of more water so that the temperature does not rise above 70° C. At this temperature 1 kilo of the powder is completely oxidized in about two hours.

6126. The advantages of this method are that the apparatus needed is of the simplest description, and can be made of almost any materials, as the products are perfectly neutral; that the gas produced is pure; and that a very large volume is yielded by a small weight or volume of the reagent (1 kilo yields 1300 liters, or 1 cubic decimeter 1770 liters). Pure aluminum filings with 1 to 2 per cent of mercuric chloride and 0.5 to 1 per cent of potassium cyanide should be used. (French Pat. 392,725, July 27, 1908.) Aluminum hydroxide is obtained as a by-product.

6127. Chem. Fabr. Griesheim-Elektron recommend a preparation consisting of finely divided aluminum (98 parts) mixed with small quantities of



FIG. 266.

mercuric oxide (1 part) and caustic soda (1 part). On treatment with water, hydrogen is evolved steadily and uniformly, 1 to 1.2 cu. m. (calculated at 0° C. and 760 mm.) being obtained from 1 kilo of the product. The mass can be kept unaltered for a long time if protected from moisture, and can be easily transported, 1 kilo occupying a volume of only 0.8 liter.²²

6128. According to Uyeno,²³ 78 to 98 parts by weight of aluminum are melted in a crucible and a mixture of 15 to 1.5 parts of zinc and 7.0 to 0.5 part of tin are added to the molten metal, after which the alloy is cast in the form of

²² Ger. Pat. 229,162, Jan. 17, 1909. In the corresponding Brit. Pat. 3188, Feb. 9, 1909, it is stated that aluminum in a divided form, such as filings, dust, chips or factory waste, is mixed with a small quantity of a compound of a metal such as mercury, which is electronegative to aluminum, and with a small quantity of an alkali or acid, or a borate, phosphate or other soluble substance. The alkali, etc., serves to generate sufficient hydrogen to reduce the mercury or other compound, which then forms an electrochemical couple with aluminum and decomposes water until the aluminum is used up.

²³ Brit. Pat. 11,838, May 18, 1912.

a plate. For each part of this alloy 0.12 to 0.025 part of mercury, or a quantity of zinc or tin amalgam containing this amount of mercury, is taken and amalgamated with the upper and lower surfaces of the plate by rubbing it in with a steel brush. The plate is then heated to as high a temperature as possible without volatilizing the mercury, until the alloy has become uniformly amalgamated, whereupon it is ready for the manufacture of hydrogen by acting on it with hot water.

6129. Jaubert²⁴ suggests that the hydrogen evolved in such industrial processes as the production of electrolytic soda, be collected, deprived of any oxygen present (as by passage over red-hot copper), dried, directed into an iron tube charged with calcium in small pieces, and heated for some hours to redness. The dark grey calcium hydride thus obtained is preserved in closed vessels. When the hydride is brought into contact with cold water, there is a violent evolution of hydrogen.

6130. Bamberger, Bock and Wans²⁵ generate hydrogen from calcium hydride which is mixed with substances such as gypsum, sodium bicarbonate, soda-lime or boric acid, which contain water or carbonic acid, but which react only when heated to about 80° C., or a higher temperature.

6131. Gases which are prepared by the action of a liquid upon a solid, for instance, hydrogen by the action of water on calcium hydride, are obtained pure and free from the water vapor which is frequently generated by the heat of the reaction, in the following manner: The solid is placed in a connected series of separate vessels, or in superposed compartments of the same vessel, and the liquid is admitted to the first, or lowest, of the series. The gas given off, along with some vapor of the liquid, passes through the next vessel, or compartment, and so through the series and leaves the last in a dry condition, the water vapor having been retained by the fresh material. When the first vessel is exhausted it is recharged and connected to the end of the series, the second vessel becoming the first. In this way the process becomes continuous.²⁶

6132. A method for preparing hydrogen is described by Helbig²⁷ which is based on the reaction of aluminum with caustic soda; 810 g. aluminum and 3600 g. caustic soda are required to furnish 1 cu. m. of hydrogen. Inasmuch as commercial aluminum and caustic soda may be regarded as 99 and 77 per cent pure, respectively, 5485 g. of the latter would be required to furnish 1000 l. of hydrogen gas. Activation of the aluminum is secured under the influence of heat, which brings about a considerable increase in the yield of hydrogen obtained when the product is subsequently treated with water.²⁸ The activation of the aluminum results from the surface amalgamation of the metal, principally upon the production of the amalgam by the reduction of the mercury compound, and from the etching action of caustic soda. The amount of hydrogen evolved is claimed to be greatly increased if the activation is effected in whole or in part with heating, either amalgamating the aluminum with heating, or etching with caustic soda in the heat, or carrying out the whole process at an elevated temperature. In the subsequent evolution of hydrogen the use of hot water is not then necessary, e.g., 50 g. aluminum filings are heated on the sand bath in a dish for about thirty minutes at 180°, and then sprinkled with 1 per cent mercuric chloride solution. The excess is poured off and washed with pure alcohol. After drying 0.2 g. of the product are drenched with about 10 cc. of a 1 per cent caustic soda solution which, after a short time, is made up to 1 liter with pure water. In twenty-five minutes about 40 cc. hydrogen are evolved. Without previous heating of the aluminum, only 31 cc. hydrogen are evolved under otherwise like conditions.

²⁴ French Pat. 327,878, Dec. 31, 1902.

²⁵ Ger. Pat. 218,257, Mar. 31, 1908.

²⁶ Jaubert, French Pat. 381,605, Nov. 14, 1907.

²⁷ *Ph. praxis*, through *Boll. chim. farm.* 1914, 53, 71; *Chem. Abst.*, 1915, 1373.

²⁸ Ger. Pat. 294,910, Jan. 27, 1916; L. Elkan Erben, G. m. b. H., *J.S.C.I.*, 1916, 336; *Chem. Abst.*, 1918, 605.

6133. The Bergius Carbon Process. Steam acts on incandescent carbon to produce hydrogen and carbon monoxide. Below 650° C. carbon dioxide instead of carbon monoxide is formed to some extent according to the reaction,



Bergius has found that this reaction occurs almost exclusively if water at a temperature of about 300° C. is allowed to act on carbon under a pressure sufficient to keep the water in a liquid state. The addition of small amounts of thallium salts is beneficial as the reaction is thereby promoted through catalytic action. In order to work under the high pressures necessitated by these considerations Bergius has made use of apparatus as shown in Figs. 267 and 268.

6134. The successful closure of the reaction chamber was attained by the use of a tapered plug forced into a seat having a taper of different angle so that the contact becomes a line

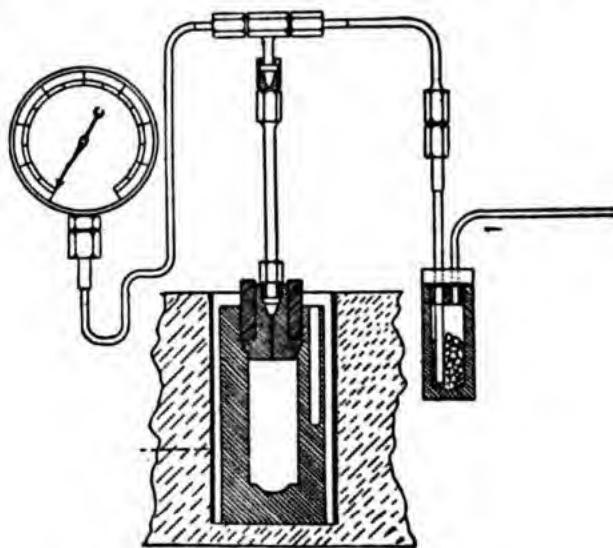


FIG. 267.

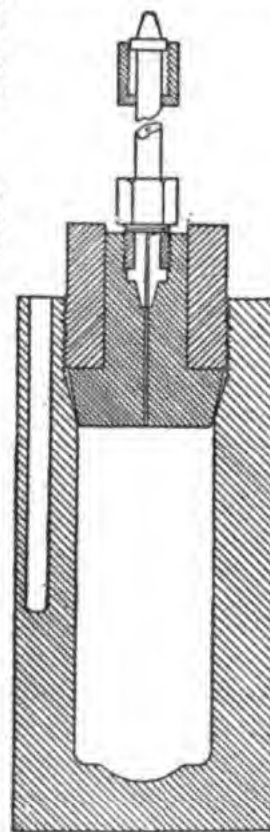


FIG. 268.

rather than a surface. (Bergius, *Die Anwendung hoher Drucke bei Chemischen Vorgängen*, Halle, 1913, 6.) A charge of say 100 kilos coke and 200 kilos water containing in solution 1 kilo of thallium chloride is placed in a strong iron vessel provided with a valve, and the vessel is heated to 340° C.²⁹ The mixture of hydrogen and carbon dioxide which collects in the upper part of the vessel is blown off through the valve at intervals of half an hour, and the carbon dioxide is absorbed by lime.

6135. Carbon-steam Process for Hydrogen. Nouvelle causes steam to act on finely divided carbon in presence of enough air to maintain the endothermic reaction. The carbon dioxide is separated in a diffusion apparatus.³⁰

²⁹ Ger. Pat. 259,030, June 24, 1911.

³⁰ Brit. Pat. 256,631, Aug. 5, 1925; *Chem. Abst.*, 1927, **21**, 2977.

6136. The Bergius Iron Process. Bergius²¹ also describes a process of continuously generating pure hydrogen from iron and water at a low temperature, from 200° to 300° C. The hydrogen is collected in the generator itself in a high state of compression and can be charged direct into cylinders. An example of his process is as follows: 50 kilograms of iron shavings and 265 kilograms iron protoxide and 50 kilograms of water are heated to 300° C. in a closed iron vessel. When the pressure reaches 150 atmospheres the release valve is opened just enough to allow the gas to escape as fast as liberated and to thus maintain the initial pressure. From the above charge 1 cu. m. of hydrogen is given off the first hour. This rate is maintained until about one-half the available gas is evolved, then the rate is somewhat slower. Common salt, iron chloride or small quantities of hydrochloric acid accelerate the reaction, and, in addition, if copper, nickel, or platinum, etc., are placed in the mass, the reaction is accelerated still more and maintains its activity until the iron is converted almost entirely into Fe_2O_3 . Thallium salts are specially good catalysts. One form of generator consists of a pressure vessel within which is a central heating tube and around the latter a series of reaction tubes, each of which can be brought in turn below a feed opening in the cover of the pressure vessel.

6136A. Posen and Bergius²¹ employ a somewhat similar method for the production of hydrogen by the action of water on metals in a closed vessel. The reaction is effected at a temperature below the sintering point of the metal or the solid reaction products, preferably below 500° C. Pure hydrogen is thus obtained in a highly compressed condition, and the yield is nearly quantitative. The addition of electrolytically conducting salts such as sodium chloride is stated to be advantageous.

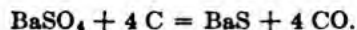
6136B. The decomposition of water by incandescent iron, as also the reduction of the resulting iron oxides by the reducing gases requires a certain temperature of the contact material, which is usually maintained by the continued heating of the furnace containing the iron material, or by passing therethrough hot combustion gases. As a result of the latter practice, the employment of a highly heated gas may occasion caking of the contact material.

6136C. This process was, at one time, in commercial use, successfully, at Hanover. We may yet see it in common use since high pressure is no longer a bugbear either to constructor or to operator. Bergius (*Zeitsch. f. angew. Chem.*, 1913, 517) states that with his process hydrogen containing less than 1/100 of a per cent of impurities may be produced. In apparatus which has been thoroughly tested at Hanover, a vessel of a capacity of 80 liters produced 12 cu. m. of hydrogen hourly. Bergius states that the construction of vessels of larger size up to a capacity of about 1 cu. m. offers no difficulty. In large plants which are arranged for proper heat utilization, Bergius estimates the cost of hydrogen at about 2 cents per cubic meter. The advantage of this process is that very pure hydrogen under high pressure may be produced at a low cost and without an expensive equipment, enabling works requiring only a small amount of hydrogen to produce this gas on the spot at low cost. The iron oxide formed by the reaction can be reduced by heating with carbon at 1000° C. and is then ready to be used a second time.

²¹ U. S. Pat. 1,059,818, Apr. 22, 1913; Ger. Pat. 277,501, Nov. 30, 1913, addition to Ger. Pat. 254,593; French Pat. 447,080, of 1912; *J.S.C.I.*, 1915, 229.

²² Ger. Pat. 286,961, Nov. 21, 1913; addition to Ger. Pat. 254,593; *J.S.C.I.*, 1916, 177.

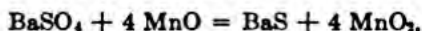
6137. In the Lahousse process ²³ coal, mixed with barium sulphate, is heated at a red heat so as to produce carbon monoxide and barium sulphide, according to the equation,



The sulphide of barium produced is then heated to redness in a current of steam, with re-formation of barium sulphate and evolution of hydrogen.



6138. Teissier and Chaillaux ²⁴ heat a mixture of barium sulphate and manganous oxide to a red heat, finally to a white heat, and pass steam under pressure over the resulting mass, when the following reactions are stated to take place:



6139, Anaërobic Fermentation. Kessener ²⁵ produces hydrogen by the following method: Waste liquor sludges, or the liquors themselves (e.g., from paper factories), are inoculated with anaërobic bacteria capable of producing methane or hydrogen, selected with special regard to the nature of the particular waste liquors employed. Suitable nutrient salts are added and the bacteria are grown under conditions which minimize the production of free nitrogen. ²⁶

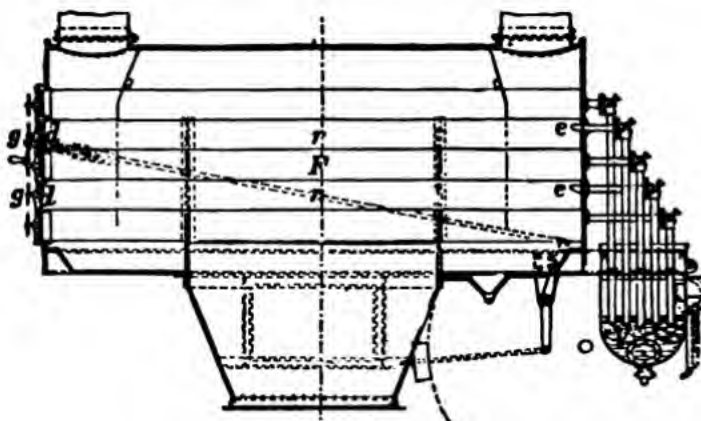


FIG. 269.

6140. When zinc dust is heated with hydrated lime, ²⁷ hydrogen is formed according to the equation,



On this reaction Majert and Richter ²⁸ have based a technical process of generating hydrogen in which they employ apparatus as shown in Fig. 269. A heating chamber *F* carries a series of horizontal tubes *r*, each of which is provided at one end with a gas eduction pipe *e*, leading to a water seal *V*, and at the other end with a removable cap. Iron or carbon may be used in place of zinc.

²³ French Pat. 361,866, Oct. 24, 1905.

²⁴ French Pat. 447,688, 1912, *J.S.C.I.*, **1913**, 234 and **1914**, 1137.

²⁵ Ger. Pat. 290,126, Feb. 7, 1914; *J.S.C.I.*, **1916**, 486.

²⁶ U. S. Pat. 1,706,707, Mar. 26, 1929, to Reilly and Blair (assigned to Commercial Solvents Corp.) deals with the separation of hydrogen from fermentation gases.

²⁷ Schwarz, *Ber.*, **19**, 1140.

²⁸ Brahmer, *Chemic de Gase*, 101.

6140A. Geuther ³⁸ gives a historical account of the preparation of hydrogen by ignition of powdered zinc, cadmium, and iron with calcium hydroxide.

6141. Separation by Diffusion. Many proposals have been made to separate hydrogen from gaseous mixtures by taking advantage of its rapid diffusion.

6142. Jouve and Gautier ³⁹ propose to pass water-gas through a porous partition, such as unglazed porcelain, in order to separate hydrogen by reason of its rapid power of diffusion. It is said that by one such operation the percentage of carbon monoxide may be reduced from 45 to 8 per cent.

6143. In Snelling's process ⁴⁰ hydrogen is separated from producer gas or other gases by diffusion through porous earthenware or alundum containers having a thin coating of platinum or palladium. The porous tube is electrically heated by resistance wires preferably to above 800°, the gas being introduced under pressure. Hydrogen diffuses through the platinum or palladium film and porous tube and is then drawn off. Several other forms of apparatus are also described. Cobalt, nickel or iron may be used instead of platinum or palladium but with decreased efficiency.

6144. The separation of the different components of a gas mixture is brought about by Wussow ⁴¹ by leading the gas over the surface of permeable or absorbing media. These media may be either solid or liquid, and different forms may be used simultaneously to separate the different constituents of a complex mixture. Moving permeable surfaces may be used to accelerate the diffusion. The diffused gas may be removed from the farther side of the diaphragm by maintaining a low pressure or by circulating an indifferent gas, such as steam, ammonia, or carbon dioxide, which afterwards can be removed by solution or condensation. Diffusion may also take place through several media in succession, each of which causes a partial separation. As an example of the process, using a layer of water as permeable medium, at 0° C., this would absorb 85.2 times as much carbon dioxide as hydrogen, and at 20° C., 49 times as much.

6145. In another diffusion process the gases containing the hydrogen are passed along one side of a permeable partition under a slight pressure, while an indifferent gas, such as sulphur dioxide or ammonia, which is easily separated from the hydrogen, is led along the other side, under a slightly reduced pressure. ⁴²

6146. In Barjot's process the gas under treatment is allowed to circulate along a porous wall, on the other side of which there is an evacuated vessel in which nitrogen may circulate and take up the hydrogen diffusing through the wall. ⁴³

6147. Elsworth ⁴⁴ proposes to separate hydrogen from water-gas by passing the latter through a centrifugal gas separator.

6148. MacDowell and Meyers heat a mixture of sulphur vapor and steam to a suitable temperature in presence of iron oxide as catalyst for a sufficient time to yield a mixture containing sulphur dioxide and hydrogen, and treat this mixture for separation of its components. ⁴⁵

6149. Epner ⁴⁶ treats coke-oven gas with an alternating electric field of high frequency and high tension. Hydrogen and liquid products are obtained.

³⁸ *Chem.-Ztg.*, 1930, **54**, 133; *Brit. Chem. Abst.*, 1930, 322.

³⁹ French Pat. 372,045, 1906.

⁴⁰ U. S. Pat. 1,174,631; *Chem. Abst.*, 1916, 1424; *J.S.C.I.*, 1916, 527.

⁴¹ Ger. Pat. 295,463, Apr. 15, 1913; *J.S.C.I.*, 1917, 330.

⁴² French Pat. 599,895, Sept. 27, 1924, to Soc. d'Etudes et de Constructions Métallurgiques; *Brit. Chem. Abst.*, 1926, 407B.

⁴³ French Pat. 601,774, May 7, 1925; Brit. Pat. 251,988, May 7, 1925. Brit. Pat. 291,576, Apr. 14, 1917, describes apparatus for separation of hydrogen by diffusion (*Brit. Chem. Abst.*, 1928, 568B).

⁴⁴ Brit. Pat. 10,581, May 5, 1906.

⁴⁵ U. S. Pat. 1,693,244, Nov. 27, 1928, assigned to Armour Fertilizer Works; *Brit. Chem. Abst.*, 1929, 172B.

⁴⁶ Brit. Pat. (application) 296,428 (convention date, Sept. 2, 1927).

6150. Carbon Disulphide and Hydrogen. Carbon disulphide and hydrogen, or gases containing hydrogen, are obtained by reaction, at temperatures above 100° , between hydrogen sulphide or sulphurous gases such as those obtained in the hydrogenation of sulphur-bearing coal or oils, and hydrocarbons such as methane, natural gas, gases from cracking, distillation of coal or destructive hydrogenation of coal, tar or oils, etc. Catalysts may be used as alumina, active carbon, silica gel, pumice or carborundum, and an electric arc or an electrically heated carbon resistance may be used to effect the reaction. Air or carbon dioxide may be added if it is desired to produce water-gas. Unchanged hydrocarbons may be further cracked or otherwise decomposed to obtain additional hydrogen.⁴⁷

ACTION OF ACIDS ON METALS

6151. One of the oldest methods of generating hydrogen and one which is to-day commonly used in the laboratory and for the production of hydrogen on the small scale is that of acting on metals with acids, iron or zinc and sulphuric acid being the materials usually employed. The cost of generation in this manner is too high to permit of large-scale operations except in those cases where hydrogen is obtained as a by-product in the preparation of metallic salts. Accordingly this method of hydrogen generation will be considered only very briefly.

6152. Carulla's process yields alkali salts, hydrogen and iron oxide, the gas being generated by the action of hydrochloric acid on iron. Instead of using water alone for the absorption of hydrochloric acid in the Le Blanc process, some or all of the receivers or towers are packed with scrap iron or mild steel, ferrous chloride being thus formed and hydrogen evolved. The chloride is then converted, by precipitation, into iron oxide⁴⁸ and, since very dilute solutions are preferable for this purpose, the absorption of the last traces of hydrochloric acid is rendered very easy by this process, the ferrous liquor plant being conveniently placed at the end of the system, and hydrochloric acid of high strength being produced, if desired, in intermediate parts of the plant.

6153. According to Barton⁴⁹ dilute sulphuric acid is allowed to act on zinc and the zinc sulphate solution produced is filtered and mixed with a solution of sodium carbonate or bicarbonate, thus giving a precipitate which is separated, washed and dried, and sodium sulphate which is also recovered.

6154. The insoluble zinc precipitate is proposed as "an excellent substitute for oxide of zinc used in the paint and rubber industries." The apparatus consists of a generating vessel, communicating with an acid tank by a feed pipe and a return pipe, and also with a gasometer and a mixing tank, the latter receiving the zinc sulphate solution from the generator and sodium carbonate solution from another vessel and communicating, in its turn, with a centrifugal separating and washing apparatus. The generator may be fitted with electrodes for the production of electrical energy.

6155. An apparatus arranged to generate electrical energy when zinc is being dissolved in sulphuric acid to produce hydrogen is set forth by Eastwick.⁵⁰ The apparatus, which is intended specially for the generation of hydrogen by the action of zinc on dilute sulphuric acid, consists of a generating chamber, with false bottom, on which rests the metal to be acted upon, and a liquid-collecting chamber situated below. The

⁴⁷ Brit. Pat. 293,172, May 26, 1927, to I. G.; *Chem. Abst.*, 1929, **23**, 1481. Cf. Pier and Winkler, U. S. Pat. 1,735,409, Nov. 12, 1929, to the I. G.; *Chem. Abst.*, 1930, 902.

⁴⁸ E. g., as in Brit. Pat. 27,302, 1908; *J.S.C.I.*, 1909, 1126.

⁴⁹ Brit. Pat. 28,534, Dec. 8, 1910.

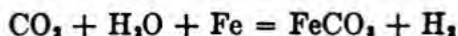
⁵⁰ Brit. Pat. 10,228, Apr. 27, 1911.

acid is delivered by gravitation into contact with the metal at a point near to, but above, the false bottom, and the salt solution produced runs through into the collecting chamber. An electrode may, if desired, be immersed in the liquid, within or below the reaction chamber, so that the apparatus may serve also as an electric cell. An apparatus described by way of example comprises superposed chambers contained within a single casing, the uppermost (containing zinc) and the intermediate chamber being provided with porous or perforated false bottoms. Acid is conducted to the first chamber by a pipe which reaches down through the upper layers of zinc into a cage having lateral perforations, and any excess of pressure forces the acid back in the supply pipe, but the zinc sulphate solution produced percolates into the lowermost chamber. A zinc rod or plate, to act as electrode, is placed above the false bottom in the first chamber and a copper electrode in the intermediate chamber, so that, with the descending liquid, an electric cell, suitable for electroplating work, etc., is produced, this also ensuring the decomposition of any free acid in the spent liquid.

6156. Hydrogen gas is obtained by Pratis and Marengo ⁶¹ by acting upon iron filings and water by gradual additions of sulphuric acid of 50° Bé., equal parts by weight being taken of each. The hydrogen produced is conducted first through water, then through a solution of a lead salt, and through a device containing diaphragms of wire gauze, to a gasometer, whence the gas traverses an insulating water valve, an elastic chamber and a second device similar to the first, when it is taken by branch pipes to the place of utilization. The arrangements described permit of the gas being produced under considerable pressure.

6157. To overcome the difficulties in the way of generating hydrogen from sulphuric acid and iron, Pratis and Marengo ⁶² propose to employ the following approximate proportions, by weight: Broken iron, 5 parts; water, 5 parts; 50° Bé. sulphuric acid, 5.8 parts; these being found to produce a pasty non-caking residue, easy to remove from the apparatus and to work up for the manufacture of ferrous sulphate or Nordhausen sulphuric acid. The apparatus consists of a generating cylinder, fitted with a valve for discharging the residue. The acid and water are run in on to the charge of iron from reservoirs at a higher level, the supply valve being controlled by the bell of the gas holder, and is self-closing when the bell sinks below a certain level; or, if the gas is to be collected in receivers at high pressure, the full charge of liquids may be added at once. Purifiers are arranged between the generator and gas holder, and an excessive rate of generation is prevented by gas checks, which cause an increase of pressure in the generator, whereby the acid is driven back in the supply pipe and the evolution of gas diminished.

6158. The reaction which takes place in the spontaneous formation of iron rust,



may be accelerated by agitation, etc., so as to become a practicable method according to Bruno ⁶³ for the production of hydrogen. Fragments of cast iron or steel or iron filings were introduced together with water into a steel bottle and carbon dioxide was passed in until the air was displaced and the liquid was saturated with the gas. The bottle was then closed by a steel cover, and placed in an apparatus where it made about 2000 revolutions per hour. There was no appreciable change in the pressure inside the vessel, and after 36 to 40 hours the gas withdrawn from the bottle consisted of pure hydrogen. At the end of

⁶¹ Brit. Pat. 16,277, July 22, 1896.

⁶² Brit. Pat. 15,509, June 29, 1907.

⁶³ *Bull. Soc. Chim.* (1907), 1, 661.

20 hours the gas consisted of about two-thirds of hydrogen and one-third of carbon dioxide.

6159. Stuart ⁵⁴ describes an apparatus for generating hydrogen by allowing acid to percolate through scrap iron.

6159A. The iron is contained in crates which are spaced away from the walls of the generator. The latter may be lined with lead, enamel, etc., to resist the action of the acid. A layer of asbestos which is held between two perforated disks is placed above and below each crate. The acid is introduced under pressure at the top of the generator and percolates through the asbestos and then through the scrap iron. This asbestos serves as a filter for the gas and for



FIG. 270.

the spent acid. Two or more crates of iron scrap may be used in each generator. Fig. 270 shows the construction of the apparatus.

6160. A method of utilizing the acid values of sodium acid sulphate or bisulphate is recommended by Becquevort and Deguide ⁵⁵ as follows: A solution of sodium bisulphate of density 20° Bé. (sp. gr. 1.16) is added to scrap iron in a suitable tank and heated by steam to 90° C. The liberated hydrogen is washed and collected in a holder. The resulting solution of ferrous and sodium sulphates is treated with an excess of powdered lime, producing a mixture of calcium sulphate and ferrous hydroxide, which is aerated to convert the latter into ferric hydroxide. The mass is filter-pressed, and the solution flowing away is concentrated to 30° Bé. (sp. gr. 1.26) and Glauber's salt separated by crystallization. The material left in the filter-press is used as a gas-purifying agent.

⁵⁴ U. S. Pat. 1,085,366, Jan. 27, 1914.

⁵⁵ Brit. Pat. 107,807, July 11, 1916; *J.S.C.I.*, 1917, 962; *Chem. Abst.*, 1917, 2947.

CHAPTER LXII

PRECAUTIONS IN HANDLING HYDROGEN. SAFETY DEVICES. PURIFICATION OF GAS

6200. The handling of electrolytically derived gases brings with it the possibility of explosions due to accidental mixing of the two gases, and to guard against serious results, at frequent intervals in the connections of the apparatus and service pipes, safety devices should be inserted.

6201. The common form of safety device is the wire-gauze arrangement of Sir Humphry Davy. It usually consists of a roll of wire gauze or a number of disks of gauze inserted in the pipe connections. Such arrangements sometimes will

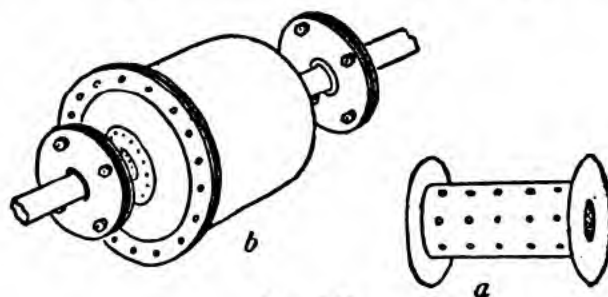


FIG. 271.

check the progress of an explosion temporarily or completely, but as a rule when an explosion wave passes along the pipe in which the wire gauze is placed, although checked temporarily by the wire-gauze obstruction, it soon heats the latter to the ignition point. Thus the gas on the other side of the gauze is ignited and the explosion wave continues on its course.

6202. When wire gauze is used preferably it should take the form shown in Fig. 271. A spool *a* carries perforations along its stem and over this wire gauze is wound to make a thick layer. The spool is placed in the holder *b* and fitted tightly in place against a rubber gasket so that gases entering one end of *b* will pass along the hollow stem, flow through its perforations and those of the gauze and make their exit at the opposite end of *b*.

6203. Glass wool obstructs explosion waves in a fairly satisfactory manner if it is inserted into the pipe connections in such a way as to fill the cross-sectional area without being packed so tightly as to greatly reduce the flow of gas. Layers of glass wool, or finely divided refractory material, such as fire-brick granules of about 20 mesh, alternated with bundles of wire gauze, may be packed

into pipes of relatively large diameter to form an excellent safety device, which is rendered even more reliable if placed in a tank of water so as to be kept cool in event an explosion wave causes ignition of the gas at the surface of the outer layer.

6204. It is stated by Schoop that under the conditions occurring in practice explosive mixtures are formed when either gas contains by volume 6 to 8 per cent of the other gas. Such an impurity may quite readily occur through injury to the diaphragm of cells of the asbestos-diaphragm type, and in constructions similar to the Garuti cell care should be taken to prevent an excess voltage which will render the diaphragms bipolar.

6205. Boynton's device for preventing the transmission of explosions is shown in Fig. 272. *A* is the gas inlet, *B* the outlet, *E* one or more perforated plates and *H* a space filled with fragments of metal.¹

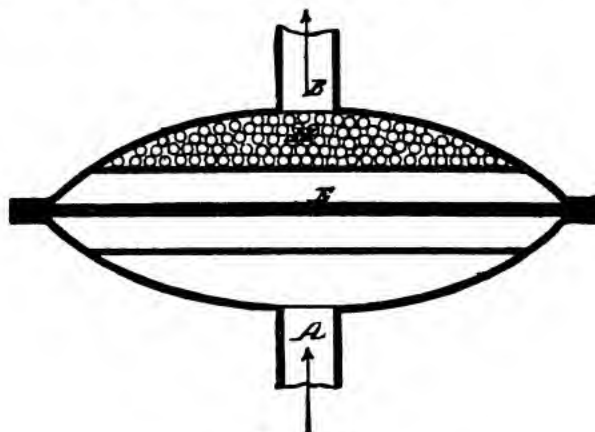


FIG. 272.

6206. For the prevention of hydrogen explosions steel wool is recommended by Ohmann.² He regards steel wool as very suitable to take up and carry off the heat developed and, by lowering the temperature in this way, preventing the spreading of an explosion. To insure against the danger of an explosion, a roll of the wool, somewhat tightly pressed together, is placed in the gas conduit. Trials with a mixture of $\frac{2}{3}$ hydrogen and $\frac{1}{3}$ air, also with the strongest explosive gas mixture $2\text{H} + \text{O}$, showed that the explosive flame or wave was checked and extinguished in contact with the wool.

6207. The various possible causes of certain fatal accidents resulting from the explosion of oxygen or hydrogen cylinders has been discussed by Bramkamp.³

6208. In most cases it is certain that an explosive mixture of hydrogen and oxygen has been introduced into the cylinder. The two most important causes of this are: (1) the use of the same compressor alternately for both gases; and (2) unsatisfactory control and attention when the gases are obtained at the same time in the electrolysis of water. Other causes which may contribute

¹ U. S. Pat. 58,055, Sept. 18, 1866. See also U. S. Pats. 713,421, 730,807, 743,064, 819,202 and 948,323.

² *Z. physik. chem. Unterricht*, 11, 272; *Chem. Zentr.*, 1912, 1, 1426.

³ *Zeit. angew. Chem.*, 1912, 536; *J.S.C.I.*, 1912, 920.

but which are unlikely in themselves to account for an explosive mixture in a full cylinder are: (1) the use of an oxygen cylinder as a hydrogen cylinder or vice versa, without previously removing all the original gas; and (2) the absorption of hydrogen by finely divided iron inside the cylinder. The various methods by which the explosive mixture when present may be exploded include: (1) ignition of oil or other combustible material in the valve or pressure gauge by the compressed oxygen; (2) local rise in temperature of the gas due to sudden closing of the valve; (3) catalytic action of finely divided iron in causing combination in the mixture and raising its temperature; and (4) pyrophoric oxidation of finely divided iron. Bramkamp is of the opinion that with suitable precautions an explosive mixture need never be put into a cylinder, and that all cylinders should be tested by analysis of their contents immediately after filling.

6209. Tubes of compressed hydrogen, accidentally contaminated with air, have been known to explode on connecting them with a manometer for the purpose of measuring the pressure of the gas. Lelarge ⁴ has found that if ordinary manometers are employed in the usual way, such explosions may occur whenever the hydrogen contains enough air to render it explosive, and the pressure is sufficiently high. The reason probably lies on the rise of temperature produced by the sudden and more or less adiabatic compression of the air in the manometer. Such accidents may be avoided by interposing, between the tube of compressed gas and the manometer, a safety-tube containing disks of metallic gauze of such mass that they are not appreciably heated by combustion of the gas mixture in the manometer. By this means the ignition of the main body of gas is prevented. Similar safety-tubes should be employed whenever a highly compressed explosive gas mixture is allowed to expand suddenly into a confined space. Before measuring the pressure of compressed hydrogen, liable to contain air or oxygen, it is advisable to determine its density, as a further safeguard.

6209A. Reducing the Inflammability of Hydrogen. Hydrogen is mixed with 0.5–2 per cent of the vapor of one or more compounds, e.g., petroleum hydrocarbons, benzene, alcohols, having a flame-propagation temperature above that of hydrogen.^{4a}

SUMMARY

6210. The majority of the numerous proposals for making hydrogen in various ways have been outlined in the foregoing for the reason that many investigators at the present time are studying the subject of hydrogen generation, and everywhere present and prospective users of hydrogen are seeking information which may enable a better understanding of the subject.

6210A. For oil hydrogenation at least four methods of generating hydrogen have found a place. These are the (1) steam-iron, (2) water-gas liquefaction, (3) water-gas and lime and (4) electrolytic systems. With the exception of the latter these all require a water-gas plant with a not wholly simple system of

⁴ *Compt. rend.*, 1912, 914.

^{4a} Koku-Kenkyujo, Brit. Pat. 294,958, July 9, 1928; French Pat. 658,515, Aug. 2, 1928; *Brit. Chem. Abst.*, 1930, 58B.

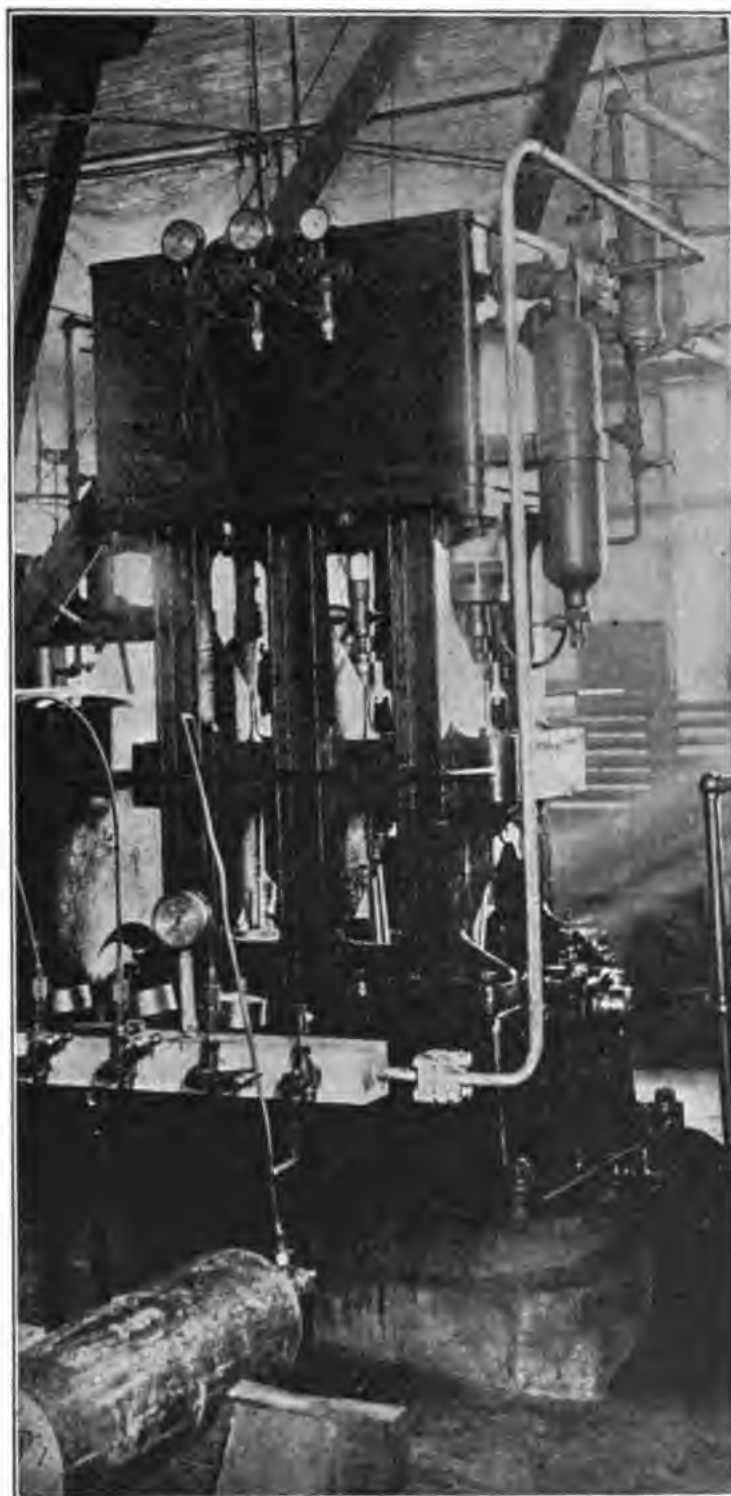


FIG. 273.—COMPRESSOR FOR COMPRESSING HYDROGEN OR OXYGEN INTO CYLINDERS.

purifiers, etc. As to the steam-iron method it may be noted that the opponents of this system claim it has been shown in practice that the iron sponge will not regenerate after a few operations and the iron retorts used are demolished all too soon by the high heat employed and have to be continually replaced. The advocates of the system claim great improvement in the matter of longevity of the iron sponge and a low cost of production. The liquefaction system, although scarcely feasible to install in a small way, is more attractive for large scale operation. The water-gas and lime system has some features in its favor, but has as yet received no extensive technical application. The electrolytic process may be called the foolproof system, as with proper safe guards against mixing of the gases and suitable safety devices, the generating plant may be operated with unskilled labor. The objections raised against it are the floor space required and the high cost of the gas. If, however, the oxygen is saved and compressed it can usually be sold at a profit which, credited against the hydrogen account, greatly reduces the cost of the latter. For small plants electrolysis has much in its favor.⁴⁶

PURIFICATION OF HYDROGEN

6211. In the previous discussion of methods of producing hydrogen various procedures of purification have been mentioned. To summarize, oxygen may be eliminated by passing the gas through heated tubes containing copper turnings; carbon dioxide by exposure to hydrated lime, carbon monoxide by contact with soda lime at 300° C. or over, in the presence of moisture, or with acid cuprous chloride; and nitrogen may be removed by exposure to heated calcium carbide. Moisture may be reduced to a negligible amount by means of quicklime, calcium chloride or other desiccating agent.

6211A. Catalysts of different types vary considerably in their resistance to impurities or catalyst poisons in the hydrogen, but the period of activity of the more reliable catalysts is at best all too short, and it may be laid down as a general rule that hydrogen free from moisture, oxygen, sulphur, phosphorus, chlorine, arsenic and cyanogen compounds should be employed. Of course there are exceptions to this, as, for example, with nickel oxide catalysts oxygen is thought not to be detrimental and in fact by some is regarded as advantageous.

6212. The Badische Anilin und Soda-Fabrik ⁵ remove traces of carbon monoxide from hydrogen by passing the gases through caustic alkali solutions at high temperatures and pressures, e.g., hydrogen containing 1 per cent of carbon monoxide is treated with (a) an 80 per cent solution of caustic soda at 50 atmospheres pressure at 260° C., or (b) a 25 per cent solution of caustic soda at 200 atmospheres pressure at 240° C.⁶

⁴⁶ The cost of hydrogen per cubic meter (1 cu. m. = 35.3 cu. ft.) produced in various ways is given by Sander, *Zeitsch. f. angew. Chem.*, 1912, 2407.

⁵ French Pat. 439,262, Jan. 22, 1912.

⁶ By heating a solution of caustic alkali under a pressure greater than five atmospheres, hydrogen is freed from sulphur and sulphur compounds. (Badische, Brit. Pat. 14,509, June 23, 1913.)

6213. Hydrogen prepared from commercial zinc and acid, is bubbled through petroleum spirit cooled by liquid air. A temperature of -110°C ., according to Renard,⁷ suffices to insure the removal in this way of all the arseniuretted hydrogen even from a rapid stream of the gas.

6214. Wentzki removes arseniuretted hydrogen from impure hydrogen by passing the gas upwards through a cylinder packed with a mixture of two parts of dry chloride of lime and one part of moist sand or other inert material. If the column of purification material be sufficiently high, the whole of the arsenic is retained. A small quantity of chlorine is set free, but can be removed by passing the hydrogen through a second cylinder packed with nearly dry slaked lime.⁸

6215. Rabenalt⁹ purifies hydrogen by passing it into a solution of iodine through which an electric current is simultaneously conducted.

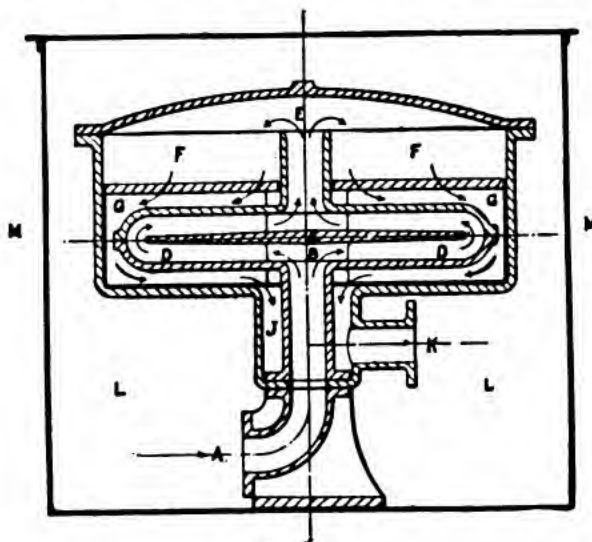


FIG. 274.

6216. For purifying electrolytic gases Knowles¹⁰ uses the apparatus as shown in Fig. 274. The gas to be purified is first passed through an ordinary washer then through an explosion trap and finally enters the purifier proper. In its entry into the purifier the in-going gas is preheated by passage around the conduit through which the out-going gas and vapor is passing. In the purifying chamber the gas passes through contact material and water vapor is formed and is condensed and removed. In the illustration the web *F* supports grids of porcelain on which the contact material is spread. Knowles states that when the apparatus is working properly no external heat is required on account of the rise in temperature caused by the condensation.

6217. The removal of sulphur from gas by the Carpenter process¹¹ involves

⁷ *Compt. rend.*, 1903, 136 (22), 1317.

⁸ *Chem. Ind.*, 1906, 405.

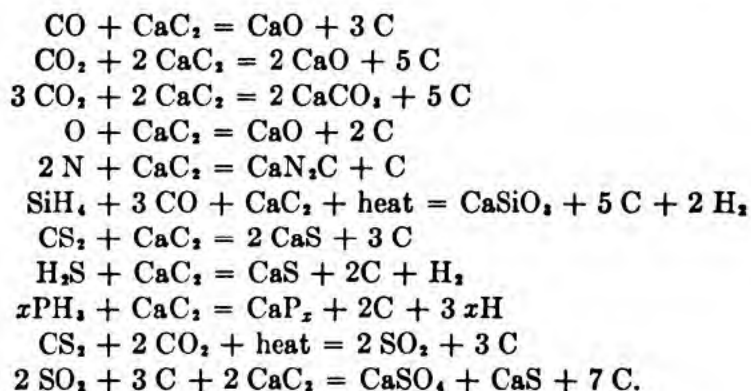
⁹ U. S. Pat. 1,034,646, Aug. 6, 1912.

¹⁰ U. S. Pat. 1,073,246, Sept. 16, 1913.

¹¹ *Jour. Ind. & Chem. Eng.*, 1914, 262.

passing the gas over reduced nickel heated to 800° to 900° F. when carbon disulphide reacts with hydrogen to form hydrogen sulphide and the latter body is absorbed in the usual manner.

6218. The treatment of water-gas to separate pure hydrogen, as described by Frank,¹² is of interest in this connection. Water-gas, previously dried as much as possible, is conducted over calcium carbide, at a temperature from 300° C. up to the melting-point of the carbide. When water-gas is conducted over carbide thus heated an absorption of all the substances associated with the hydrogen takes place. Carbon monoxide or dioxide forms with the carbide, lime or carbonate of lime and carbon. The nitrogen is likewise absorbed. The hydrocarbons are decomposed when passed over the heated lime-carbon material with the separation of carbon. The action of the carbide on various gases is indicated by Frank in the following reactions:



6219. Almost chemically pure hydrogen is ultimately obtained as the final product. Carbon monoxide or dioxide may be previously entirely or partially removed from the water-gas by mechanical separation of the constituent gases to relieve the carbide from the duty of separating the major part of the gases. If the water-gas is produced at a high furnace temperature and contains in addition to hydrogen almost exclusively carbon monoxide and only a little carbon dioxide, the mechanical separation is preferably effected by conducting the water-gas, which has been suitably cooled, into a Linde's air-liquefaction machine or other similarly constructed apparatus to liquefy the carbon monoxide; the dioxide and small quantities of silicon hydride, etc., being obtained solid, whereas the hydrogen remains gaseous and can be separated and conducted away. If the water-gas is produced at a low temperature, and if little carbon monoxide and principally carbon dioxide are obtained in addition to hydrogen, the previous mechanical separation may be effected by the water-gas being cooled down to a temperature below that of the congealing or liquefying point of the secondary constituents of the water-gas (carbon dioxide, carbon monoxide, etc.), these secondary constituents being separated in this manner in a

¹² U. S. Pat. 964,415, July 12, 1910.

solid or liquid form from the hydrogen which is obtained. After the previous mechanical separation of the secondary gases, the hydrogen which contains some remnant of other gases, as carbon oxides, silicon hydride, hydrogen sulphide, phosphoretted hydrogen, nitrogen, carbon disulphide, and hydrocarbons, is then subjected to a final purification by conducting it over carbide. Before being passed over the carbide, the water-gas may be freed from carbon dioxide and monoxide by treatment with lime and cuprous chloride solution respectively.¹³

6220. Bosch and Wild¹⁴ have found that by treating hydrogen under pressure exceeding five atmospheres with a hot solution of fixed caustic alkali, sulphur and compounds containing sulphur can be practically completely removed.

The concentration of the alkaline solution and the temperature and pressure employed can be varied within wide limits. As an example, caustic soda solution of from 10 to 50 per cent can be employed at a temperature of from 150° to 225° C. and a pressure of 50 atmospheres. As a rule, if higher pressures be employed, the gases can be passed through the caustic alkali solution with a greater velocity while still effecting a total separation of all sulphur and sulphur compounds.

6221. A purifier for separating dust and sulphur compounds from producer-gas, water-gas, and the like is described by Berlin Anhaltische Maschinenbau¹⁵ as follows: Within and spaced away from the wall of the purifier is a retort packed with turnings of iron or other metal capable of combining with sulphur compounds. Except at the two ends the wall of the retort is porous. The gas enters the purifier, and passes through the porous wall of the retort, which retains dust, etc. A blast of air may be passed into the purifier to bring it to and maintain it at the requisite temperature for the retention of the sulphur compounds by the iron turnings.

6221A. Hydrogen containing oxidizable impurities, e.g., carbon monoxide or hydrocarbons, and also reducible impurities, e.g., sulphur or phosphorus compounds, is humidified and mixed with water vapor and with sufficient oxygen and hydrogen to combine with the impurities, and then passed under pressure over charcoal at not above 600°, the conversion products of the impurities then being removed by known means.¹⁶

6222. It is stated by the Badische Company¹⁶ that carbon monoxide can be very quickly and effectively removed from gas mixtures by means of ammoniacal cuprous chloride solution under pressure.

6223. The solutions contain, in 1 liter, considerably more than 60 grams of ammonia gas in the form of free base or carbonate. Iron apparatus or parts in motion are not injured by this solution so that high pressure can be employed, where stoneware and lead are not suitable. Ammonia is supplied as it is lost, the solution is kept in circulation between the absorption and a lower pressure chamber where the carbon monoxide is removed, and any oxidation of copper is corrected by the carbon monoxide before it is removed. A suitable solution is prepared by mixing 200 kilograms of cuprous chloride, 250 kilograms of ammonium chloride, 500 kilograms of 25 per cent ammonium hydroxide and 500 kilograms of water. Operating at pressures above 100 atmospheres very small amounts of carbon monoxide may be removed from gases (such as hydrogen containing carbon monoxide) in a short time.

6224. The absorption of carbon monoxide from oxygen-free gas mixtures by ammoniacal cuprous chloride solutions is carried out by the Badische Company¹⁷ with an addition of

¹³ French Pat. 371,814, Nov. 26, 1906.

¹⁴ U. S. Pat. 1,133,087, Mar. 23, 1915.

¹⁵ Ger. Pat. 271,122, Dec. 12, 1912; U. S. Pat. 1,129,558; *J.S.C.I.*, 1914, 472.

¹⁶ Soc. d'Etudes Minières & Industrielles, Brit. Pat. 302,306, Nov. 16, 1928; *Brit. Chem. Abst.*, 1930, 143-4B.

¹⁷ Ger. Pat. 282,505, Nov. 19, 1913; *Chem. Abst.*, 1915, 2299; see also Brit. Pat. 9,271, Apr. 14, 1914.

¹⁷ *Chem. Abst.*, 1917, 873; Austrian Pat. 72,240, Aug. 10, 1916.

oxygen to the gas sufficient in amount to prevent the separation of copper but not in such a quantity as to cause any marked oxidation of carbon monoxide.

6225. A method of freeing gases from carbon dioxide present as impurity is given by Soc. L'Air Liquide,¹⁸ which consists in subjecting the impure gas first to a physical purification by solution under pressure in water and then to a chemical purification by the action of a purifying reagent dissolved in the water.

6226. The process is applicable to the removal of carbon dioxide from water-gas or water-gas modified by catalysis or by passage over hydrated lime, prior to liquefaction of the gas. The process is effected by bringing the compressed gas into contact with a counter-current of water in a tower, at the upper portion of which is introduced a small quantity of lime or caustic soda. The dissolved gas may be subsequently removed from the liquid by relieving the pressure thereon, and, when lime is used, the precipitated carbonate may be filtered off and the water returned to the tower.

6227. For the purpose of freeing hydrogen from carbon dioxide by scrubbing with water or with an aqueous solution under pressure, the pressure is released from the resulting solution in separate stages, so that a gas richer in hydrogen than that in solution is first obtained. This may be again compressed and retreated. Various pressures up to 200 atmospheres may be used in the different stages of the process.^{18a}

6228. In a process for the absorption of gases by liquids, under pressure, with subsequent regeneration of the absorbent by relieving the pressure, Ges. für Linde's Eismaschinen¹⁹ absorption is effected under as high a pressure as possible and the absorbed gas subsequently released by producing a partial vacuum in the absorption vessel and simultaneously passing through it a current of gas in which the concentration of the absorbed gas, if this be present, is lower than corresponds to its partial pressure, in the gas above the solution. It is stated that by this process the absorption of carbon monoxide in cuprous chloride solution, which hitherto has proved impracticable, may be used with good results, e.g., for the production of hydrogen free from carbon monoxide.

6229. To remove oxygen from gaseous mixtures, Siemens and Halske²⁰ pass the gases over a metal heated to incandescence, the metal being one, such as zirconium or titanium, the oxide of which is not reduced by hydrogen or carbon monoxide at the temperature of working. In practice gases to be freed from oxygen frequently contain hydrogen or oil vapors. By the process described, it is stated that oxygen can be removed from such gases without formation of steam.

6230. Ueno and Kimura²¹ purify by-product hydrogen by treatment with metallic copper, a cuprous salt and ammonium hydroxide, with or without the addition of another ammonium compound. Ueno²² employs colloidal platinum, palladium, iridium or osmium in an aqueous vehicle containing an organic body such as sugar or glycerine, gum arabic and soap.

6231. When working with hydrogen at raised temperature and under pressure in iron vessels, according to Bosch²³ if the iron contains carbon the strength of the vessel suffers to such an extent that after a very short time it is no longer able to withstand the higher pressure which is being employed, due to the action of the hydrogen upon the carbon. The use inside such iron tube of a lining which is chemically not acted upon by hydrogen is of little value, since, when high temperatures are employed, practically all substances are pervious to hydro-

¹⁸ Brit. Pat. 15,053, June 23, 1914.

^{18a} Gordon and Imperial Chem. Ind., Ltd., Brit. Pat. 311,299, Jan. 31, 1928; *Chem. Abst.* 1930, 928.

¹⁹ Ger. Pat. 289,106, Mar. 29, 1914; *J.S.C.I.*, 1916, 523.

²⁰ Ger. Pat. 279,132, June 28, 1913; *J.S.C.I.*, 1915, 230.

²¹ *Chem. Abst.*, 1918, 208; Japanese Pat. 31,292, July 10, 1917.

²² Japanese Pat. 31,291, July 10, 1917.

²³ U. S. Pat. 1,188,530, June 27, 1916.

gen under pressure. Although the quantity of hydrogen which diffuses through the walls of the tube is only minute in comparison with the total quantity of gases treated in such tube, yet in course of time this small quantity is sufficient to act on the carbon contained in the iron of the tube to such an extent as to deteriorate the resisting power of the tube.

6232. Bosch states that he can work conveniently with flowing hydrogen under continuous pressure and at raised temperatures if the vessel in which the reaction is being carried out and within which the high pressure is being maintained, be surrounded by some kind of structure which is capable of supporting the inner vessel, but which itself readily allows any gas to escape which may diffuse through the walls of the inner vessel. This can be effected by surrounding the inner vessel with a series of steel rings, or a suitable network of bars, or the inner tube may be covered with a second tube which is perforated, the essential condition being that the outer tube, which is supporting the inner tube, is not impervious to the hydrogen which diffuses through the inner tube at the high temperature and pressures employed. It is most convenient to construct the outer perforated tube, network or rings, of steel, while the inner tube, in which the hydrogen is contained under pressure and heat, may be constructed either of steel, or of some material which does not contain carbon, such as wrought iron (practically free from carbon), nickel or silver.

6233. Reactions in which hydrogen is involved under pressure and at high temperatures are carried out in an apparatus comprising an exterior (metallic) receiver, capable of supporting the pressure, and an interior receiver (e.g., of glazed porcelain, glass, quartz, etc.), capable of resisting the chemical action and the diffusion of the hydrogen. Or, the reaction is allowed to take place in an inner metallic or non-metallic porous receiver, which is separated from the outer wall, supporting the pressure, by an alloy or composition capable of resisting the chemical action and diffusion of the hydrogen.²⁴

6234. Pier²⁵ describes an apparatus for effecting reactions with hydrogen under pressure. To prevent leakage of hydrogen, a layer of molten Wood's metal or other readily fusible alloy is maintained between the upper wall and the outer casing of the vessel (which may be of steel). The inner wall may be of porcelain or metal. The apparatus will withstand 150 atmospheres pressure without leakage.

EFFECTS OF THE PRESENCE OF HYDROGEN IN ELECTROLYTIC OXYGEN

6235. Experiments conducted by the Bureau of Mines tend to indicate that, at atmospheric pressure, mixtures of oxygen and hydrogen containing less than 10 per cent by volume of hydrogen are inflammable but not explosive. Teras and Plenz find at least 30 per cent of oxygen is required for explosion. The electrolytic industry for making oxygen and hydrogen, as a general rule, attains on an industrial scale the generation of both oxygen and hydrogen at purities well above 99 per cent. Hydrogen containing but 1 per cent of oxygen apparently need not be considered a hazardous product, as the oxygen in such a mixture, it is claimed, cannot be made to combine with the hydrogen to produce an explosive reaction.

6236. The attention of the Bureau of Mines²⁶ has been directed to a series of explosions of oxygen made by the electrolytic process in which life has been lost, as a result of hydrogen being mixed with oxygen. Rice, of the Bureau of Mines, reports that this is due to improper design in the manufacturing apparatus, i.e., the cells and electrical connections; to insufficient safeguards connected with the electric apparatus, the polarity suddenly and unexpectedly shifting; to the manufacture of oxygen without frequent analyses; and to incompetent or ignorant attendants. Unfortunately, certain makers of oxygen-manufacturing apparatus have advertised that any laborer can take care of their

²⁴ *Chem. Abst.*, 1915, 28; French Pat. 469,391 and First addition, Mar. 7, 1914.

²⁵ U. S. Pat. 1,159,865, 1915.

²⁶ *Met. Chem. Eng.*, 1917, 402.

apparatus. It is believed that the manufacture of electrolytic oxygen can be carried on in a manner to make it entirely safe. Nevertheless, certain tanks from one batch caused three widely separated explosions in California, killing seven men in all, and an analysis of gas from a tank filled at the same time showed that it contained over 50 per cent of hydrogen.

6237. The California Commission, after thorough investigation as to the cause of three explosions, limited the hydrogen content in oxygen containers to 2 per cent.²⁷

6238. Wohler²⁸ referring to the regulations which have been enforced in Germany with regard to the filling and use of compressed gas cylinders for oxygen and hydrogen gases, gives details of some explosions to show that in spite of all these precautions accidents due to carelessness and negligence are of frequent occurrence.

6239. The most disastrous of these, in which three men were killed and many were injured, occurred at Darmstadt. An empty oxygen cylinder of 210 cu. ft. capacity was filled with hydrogen, but the error was discovered before the gas was used and the cylinder was returned to the compressed gas works. Without emptying the cylinder, the men in charge of the oxygen-filling machinery filled the cylinder to its maximum capacity with oxygen, and when the cylinder arrived at the railway workshops the second time, and was put into use, it burst. Owing to the shortage of copper, during the war, the connecting gas couplings used at the filling works were made of iron or steel. The rule with regard to right- and left-handed threads to the cylinder fittings for the different gases was, therefore, easily evaded, for a steel or iron screw may be externally threaded on a brass connecting piece whatever the thread may have been on this originally. The regulations with regard to the use of distinctive colors for the cylinders containing the two gases were also often ignored, owing to labor shortage and similar difficulties, and cylinders were used indiscriminately for oxygen or hydrogen, without regard to their color or markings. As a precaution against similar accidents and explosions Wohler recommends the application of the Haber test for explosive gases before the gas from any cylinder is used, or the still more simple soap-bubble test, which consists in blowing a bubble with the gas from the cylinder, and then applying a light. These tests, however, are of little value if left in the hands of the workmen, since negative results can easily be obtained with them.

6240. Hammond²⁹ describes an apparatus that prevents polarity reversal by use of an automatic switch which completes the connection with the cells only when the normal speed of the generator is reached. Reversal of phase is prevented by use of a polarized relay connected to a special shunt which provides for a single-pole relay in the control circuit.³⁰

²⁷ Brownell, *Eng. Record*, 1917, 594.

²⁸ *Z. angew. Chem.*, 1917, 30, 174; *J.S.C.I.*, 1917, 917.

²⁹ *Machinery*, 23, 1070, 1917; *Chem. Abst.*, 1917, 2860. Apparatus for the determination of purity of oxygen by absorption with metallic copper and of hydrogen by the combustion method are illustrated. Causes of explosions and precautions to be observed are given.

³⁰ An explosion arrester involving the use of a water seal is described by Ellis, U. S. Pat. 1,170,055, Feb. 1, 1916. Oil-hardening tank explosion. (Byrne, *Chem. Trade J.*, 58, 164, 1916; *Chem. Abst.*, 10, 1271.) An explosion occurred May 22, 1915, in one of six tanks employed by Messrs. Ardol, Ltd., Selby, Yorks, in converting oil into a solid by means of hydrogen. Each tank was fitted with 3 vertical coils of copper tubing forming an endless circuit through which hot water was passed. Its temperature normally was about 290° and its pressure 2000 lb. per sq. in. The oil in the tank was heated to a temperature of about 260° and the hydrogen, at a pressure of 5 lb. per sq. in. was sent from the bottom upward through the tank to the cleansing plant. The accident is found to have been due to a leakage from the copper coil producing an undue pressure in the tank.

CHAPTER LXIII

ADDENDA

Since the major portion of the text of this book was placed in print additional material has come to hand which has received brief notice in the following appended items. These range through most of the subjects treated in the preceding chapters.

6300. Ortho- and Para-Hydrogen. Bonhoeffer and Harteck have shown that the change in the specific heat of hydrogen with temperature is due to the presence in molecular hydrogen of two components which have been termed ortho- and para-hydrogen. They have also shown that the transformation between the two forms can be catalyzed. [*Z. physik. Chem.*, Abt. B, 1929, **5**, 292; *Chem. Abst.*, 1930, 279.] At the ordinary temperature hydrogen comprises a mixture of one part of para-hydrogen to three parts of ortho-hydrogen, at the temperature of liquid air the ratio is about 1 : 1, while at 20.4° Abs. it is practically pure para-hydrogen. The triple points of the two forms are slightly different, as also are physical properties such as specific heat and thermal conductivity. [Bonhoeffer and Harteck, *Z. Elektrochem.*, 1929, **35**, 621; *Brit. Chem. Abst.*, 1929, 1372A.] According to the theory of allotropy, there are several possible T-X diagrams for systems of ortho- and para-hydrogen. Depending on their mutual solubilities, there may be instead of a triple point, a pressure-temperature curve along which the solid phase melts under its own vapor pressure. [Smits, *Proc. Acad. Sci. Amsterdam*, 1929, **32**, 603-9; *Chem. Abst.*, 1930, 279.] To make para-hydrogen, ordinary hydrogen is absorbed to the point of saturation on A-charcoal at atmospheric pressure and at the temperature of liquid hydrogen. When the gas is pumped off after a few minutes it is 99.7 per cent para-hydrogen, recognized by its increased conductivity. In their chemical and electrochemical behavior the two modifications show no difference. [Bonhoeffer and Harteck, *Z. physikal. Chem.*, Part B, 1929, 113; *Brenn.-Chem.*, 1929, 369.] Reversion from para- to ordinary hydrogen can be brought about by irradiating the quartz conductivity vessel with the rays from a well-cooled mercury lamp, and the change in heat conductivity followed at the same time with a sensitive bridge arrangement. [Senftleben, *Z. physikal. Chem.*, Part B, 1929, 169; *Brenn.-Chem.*, 1929, 370.] Smits regards the proof of the existence of para- and ortho-hydrogen as a proof of the principles on which the theory of allotropy is based. [*Physik. Z.*, 1929, **30**, 425-7; *Chem. Abst.*, 1929, 4855.] A calculation of the probability of transition of the symmetrical into the anti-symmetrical hydrogen by spontaneous radiation. [Bonhoeffer and Harteck, *Z. physik. Chem.*, 1929, Abt. B, **4**, 113-41; *Chem. Abst.*, 1929, 4383.] Weber gives a brief summary of the investigations of Eucken, and Bonhoeffer and Harteck on the modifications of hydrogen. [*Archiv. Chem. Farm.*, 1930, **4**, 16-20; *Chem. Abst.*, 1930, 2655.]

6301. Atomic Hydrogen. Atomic hydrogen from a Wood tube was passed through a straight tube, and the degree of dissociation at various points was determined by measuring the heat effect on platinum foil. The rate of recombination was found to conform to the three-body mechanism for exothermic binary reactions. [Smallwood, *J. Am. Chem. Soc.*, 1929, **51**, 1985-99; *Chem. Abst.*, 1929, 4397.] Dissociated water vapor seems to be more reactive than atomic hydrogen, in that it will reduce metallic salts which are not reduced by atomic hydrogen. Also the active gas is more easily

prepared from water vapor than from hydrogen. It has been suggested that there is another active constituent in the gas, probably the hydroxyl-radical. [Urey and Lavin, *J. Am. Chem. Soc.*, 1929, **51**, 3290-3.] The disappearance of hydrogen in discharge tubes is attributed to the effect of atomic hydrogen. The combination of atomic hydrogen takes place on the surface of the glass, which becomes heated and gives up carbon monoxide and carbon dioxide. These gases react with hydrogen. If water vapor is excluded from the tube no disappearance of hydrogen is observed. [Delaplace, *Compt. rend.*, 1929, **189**, 849-50; *Brit. Chem. Abst.*, 1930, 45A.] The two quantum excited states of the hydrogen molecule. [Kemble and Zener, *Phys. Rev.*, 1929, **33**, 512-37; *Chem. Abst.*, 1929, 4878.] Copaux discusses the properties and production of active nitrogen and hydrogen. The prediction of and experimental evidence for the existence of ortho- and para-hydrogen are outlined. [*Chim. et Ind.*, 1930, **23**, 267-72; *Brit. Chem. Abst.*, 1930, 524A.]

6302. Reactions of Atomic Hydrogen. Atomic hydrogen, prepared by Wood's method, was allowed to react with organic compounds. Azoxybenzene is reduced to aniline through the intermediate stages of azobenzene and hydrazobenzene. Dyes are immediately decolorized, but they partly regain their color on exposure to air; indigotin is reduced to indigo-white. Benzoic acid and acetamide catalyze the recombination of atomic hydrogen, but are not attacked themselves; formic acid also promotes this recombination, but is itself slightly reduced to formaldehyde in the process. Acetaldehyde is polymerized to paraldehyde. [Urey and Lavin, *J. Am. Chem. Soc.*, 1929, **51**, 3286-90; *Brit. Chem. Abst.*, 1930, 46A.] Bonhoeffer and Harteck describe the reaction of atomic hydrogen with hydrocarbons. [*Z. physik. Chem.*, 1928, **139**, 64-74; *Chem. Abst.*, 1929, 5154.] Active hydrogen, passed over metallic lead, forms a lead hydride which decomposes at red heat with formation of a lead mirror. Decomposition also takes place during condensation. [Schultze and Müller, *Z. physik. Chem.*, 1930, **6B**, 267-71; *Chem. Abst.*, 1930, 2036.] Nagel and Tiedemann describe an apparatus for studying the action of atomic hydrogen, obtained in a Geissler tube according to the Wood-Bonhoeffer method, on organic material. With active hydrogen oleic acid is first changed into stearic acid and then polymerization occurs. [*Wiss. Veröffentlich. Siemens-Konzern*, 1929, **8**, 187-98; *Chem. Abst.*, 1930, 2363.]

6303. Adsorption. Constable has studied the kinetics of the hydrogenation of ethylene on a copper catalyst of measured surface area. The proportions of adsorbed gases, the activity of the catalyst and the area of the surface changed with repeated oxidation and reduction. [*Z. Elektrochem.*, 1929, **35**, 105-10; *Chem. Abst.*, 1929, 4397.] The isotherms of adsorption of hydrogen, ethylene and ethane by catalytic nickel have been studied by Foresti. Theoretical considerations and the experimental data together favor the idea of the "heterogeneity" of the surface of the catalyst. [*Gazz. chim. ital.*, 1929, **59**, 243-58; *Chem. Abst.*, 1929, 4615.] The differential heat of adsorption for hydrogen of various samples of platinum-black has been measured. The heat of adsorption is of the order of 30,000 g.-cal. Catalytic activity runs parallel to the adsorption characteristics of these samples of platinum-black. [G. B. Taylor, Kistiakowsky, and Perry, *J. Phys. Chem.*, 1930, **34**, 748-52; *Brit. Chem. Abst.*, 1930, 522A; *Chem. Abst.*, 1930, 2663.] Benton and White have studied the adsorption of hydrogen by reduced nickel at pressures from zero to one atmosphere and at temperatures from 110 to -210°. They conclude that at the lowest temperatures the adsorption is of the "secondary," or ordinary molecular type, while at higher temperatures a progressively larger fraction of the nickel surface is capable of holding the hydrogen by adsorption of the "primary" type, involving a marked activation of the gas. [*J. Am. Chem. Soc.*, 1930, **52**, 2325-36.] Catalytic combination of hydrogen with ethylene or carbon monoxide but not with nitrogen occurs appreciably over metallic cesium at room temperature, but more rapidly at 200°. The rate of combination is much retarded by the gradual formation of cesium hydride. It is concluded that only adsorbed hydrogen is available for hydrogenation, and that hydride formation serves merely to diminish the free surface. [Hill and Kistiakowsky, *J. Am. Chem. Soc.*, 1930, **52**, 892-4.]

6304. Catalyst Poisons. Sulphur is found to be less poisonous to nickel catalysts than arsenic. [Moshkin, *Masloboino-Zhirovoe Delo*, 1928, No. 10, 16-7; *Chem. Abst.*, 1929, 4839.] Catalysis of the hardening of fatty (sardine) oils by nickel is retarded by the presence of minute quantities of nitric acid and ammonia. Nitrogen, ethylene, methane, and carbon dioxide have no effect. [Ueno and Yukimori, *J. Soc. Chem. Ind., Japan*, 1929, 32, 318-21B; *Brit. Chem. Abst.*, 1930, 292B.] Ueno tried the effect of 65 different organic compounds as negative catalysts in the hydrogenation of soya bean oil with nickel catalysts. Compounds which are poisons to the human body act as negative catalysts for nickel. Anesthetics, such as barbitol and dial, which do not contain halogens, sulphur or phosphorus have a narcotic action on the nickel catalyst. [*J. Soc. Chem. Ind., Japan*, 1926, 31, 303-6B; *Chem. Abst.*, 1930, 3123.] As little as 2 per cent of nitrogenous material in crude cod-liver oil and 1 per cent blood or the presence of free fatty acids diminishes the absorption of hydrogen by the oil. [Pincass, *Seifensieder-Ztg.*, 1929, 56, 248; *Chem. Abst.*, 1930, 2318.] In the formation of atomic hydrogen, glass walls may be permanently poisoned by covering them with oily phosphoric acid. The protective action depends on a definite partial pressure of water in the hydrogen. Admixture of oxygen as a protective gas is effective only after formation of water. [von Wartenberg and Schultze, *Z. physik. Chem.*, 1930, 6B, 261-6; *Chem. Abst.*, 1930, 2036.] Andrews has noted the various impurities in oils which act as catalyst poisons during their hydrogenation. [*Chem. Trade J.*, 1929, 84, 277-8, 302-3, 351-2, 369-70; *Chem. Abst.*, 1930, 1530.]

6305. Combination of Gases on Metallic Surfaces. The combination of hydrogen and oxygen on the surface of platinum has been studied by Donnelly and Hinshelwood [*J. Chem. Soc.*, 1929, 1727-33; *Chem. Abst.*, 1929, 5398] by means of a wire heated below the temperatures at which explosion takes place. They affirm the existence of active centers of different kinds on platinum wire. There are no definite indications of chain reactions extending out from the wire. The rate of combination of hydrogen and oxygen on the surface of nickel is proportional to the partial pressure of hydrogen and independent of that of oxygen down to 50 mm. The hypothesis that the combination takes place by molecules of hydrogen striking adsorbed molecules of oxygen is confirmed. [Donnelly, *J. Chem. Soc.*, 1929, 2438-44; *Brit. Chem. Abst.*, 1930, 42A.] When a surface of metallic silver is brought into contact with gaseous oxygen in sufficient quantity to form more than a complete unimolecular layer of oxide, it becomes coated almost immediately with a film of oxide. This oxide, formed at a low temperature, is a much more effective catalyst than that formed at a high temperature and is also more easily reduced by hydrogen. There appear therefore to be two forms of silver oxide, and it is assumed that in the active film, formed at a low temperature, some of the silver oxide molecules are in relatively unstable positions, but that on raising the temperature the arrangement becomes more stable and the film in consequence less active chemically. [Chapman and Hall, *Proc. Roy. Soc.*, 1929, A, 124, 478-93; *Brit. Chem. Abst.*, 1929, 1020A.]

6306. Adsorption on Platinum. Measurements of adsorption of fumaric, maleic, succinic, itaconic, mesaconic, and citraconic acids on platinum-black show that the solubility of these acids in a given solvent plays only a secondary part in their adsorption, which is determined primarily by their structure. The adsorption is increased by the presence of an ethylenic linking, except in the cases of fumaric and maleic acids in ethereal solution. In the case of isomeric acids, the more readily reducible *cis*-isomeride is more strongly adsorbed than is the *trans*-isomeride. [Platanov, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 1055-64; *Brit. Chem. Abst.*, 1930, 28A.] In the reaction between carbon dioxide and hydrogen on the surface of platinum, Srikantan has found that the reaction starts with a high velocity, but this falls rapidly to a low and steady value, owing to the poisoning of the more active centers on the surface by the carbon monoxide that is formed. Comparative experiments with platinum wire scratched with emery show that a rough surface is more active than a smooth or sintered one. [*J. Indian Chem. Soc.*, 1929, 6, 931-47; *Brit. Chem. Abst.*, 1930, 551A.] The active catalyst in the

reaction between carbon dioxide and hydrogen on a platinum wire coated with barium oxide is a complex of barium oxide and barium carbonate. The reaction is unimolecular. Carbon dioxide is readily adsorbed by the surface, and the rate of reaction rises with the carbon dioxide present up to a partial pressure of 300 mm., whereas excess hydrogen diminishes the rate of reaction. [Srikantan, *J. Indian Chem. Soc.*, 1929, 6, 939-67; *Brit. Chem. Abst.*, 1930, 551A.] The decomposition of formic acid into carbon dioxide and hydrogen at 100° C. in presence of salts of osmium, platinum, iridium, rhodium and palladium is preceded by a reduction of the noble metal salt to metal. The catalytic decomposition is due to adsorption of hydrogen by the metals. [Müller and Loerpabel, *Monatsh.*, 1929, 53 and 54, 825-51; *Chem. Abst.*, 1930, 290.]

6307. Reduction of Metal Oxides by Hydrogen. Taylor and Starkweather have investigated the rate of reduction of iron, copper, zinc and nickel at temperatures below 500° by measuring the volume of hydrogen consumed. Ferric oxide gel is reduced to ferrous-ferric oxide at 350° and to metallic iron at 450°. Ignited ferric oxide is not reduced at an appreciable rate at 350° but goes to metal at 450°. Foreign metal interfaces with iron oxide accelerate the reduction to iron. [G. B. Taylor and Starkweather, *J. Am. Chem. Soc.*, 1930, 52, 2314-25.] In order to determine the lowest temperatures at which oxides show reduction, dry electrolytic hydrogen was passed over a known amount of oxide heated at a known temperature. The loss in weight of the oxide was measured, and the water formed was also absorbed and weighed. Appreciable reduction is noticed first at 140°-1° with cupric oxide, 310° with zinc oxide, 185° with litharge, 280° with cadmium oxide and 185° with arsenious oxide. [St. John, *J. Phys. Chem.*, 1929, 33, 1438-40; *Chem. Abst.*, 1930, 2365.]

6308. Contact Isomerization. Certain cases have been noted of isomerization of organic compounds induced by contact with a catalyst and in the presence or absence of hydrogen. For example, *spirocyclodecane* is isomerized in presence of platinized charcoal and hydrogen at 190° to a compound, $C_{10}H_{18}$. Isomerization occurs more slowly in an atmosphere of carbon dioxide. The isomer does not become dehydrogenated in presence of palladized asbestos or platinized charcoal at 300°. [Zelinski and Schuikin, *Ber.*, 1929, 62B, 2180; *Brit. Chem. Abst.*, 1929, 1287A.] Platinov has found that maleic acid is partially converted into fumaric acid by adsorption on platinum-black. This is also true of other *cis-trans*-isomerides. [*J. Russ. Phys. Chem. Soc.*, 1929, 61, 1055-64; *Brit. Chem. Abst.*, 1930, 28A.] Treatment of an alcoholic solution of Δ^2 -tetrahydroanthraquinone with colloidal palladium in the absence of air, causes migration of the δ -atoms to the carbonyl group, with formation of 9, 10-dihydroxy-1, 4-dihydroanthracene. [Diels, Alder and Stein, *Ber.*, 1929, 62B, 2337; *Brit. Chem. Abst.*, 1929, 1303A.] The shifting of the double bond in an aliphatic compound from the end carbon atom has been effected at a relatively low temperature without pressure. 2, 6-Dimethyl-7-octene slowly passed (2 drops per minute) in a slow current of carbon dioxide over palladium-asbestos at 200° is completely changed into 2, 6-dimethyl-6-octene (dihydrobupuleurolene). [Zelinski and Levina, *Ber.*, 1929, 62B, 1861-3; *Chem. Abst.*, 1929, 5466.] When catalytically reduced under the influence of finely divided nickel, *cycloheptene* undergoes rearrangement, methylcyclohexane being obtained. [Rozanov, *J. Russ. Phys. Chem. Soc.*, 1929, 61, 2313-8; *Brit. Chem. Abst.*, 1930, 602A.] The products obtained by passing the vapors of carane, *cyclofenchene* and tricyclene, mixed with hydrogen, over platinum catalyst at a temperature of 160° and at atmospheric pressure have been identified and found to be the result of the breaking of one of the rings of the original compound. A similar study has been made of the breaking of the rings and the formation of double bonds when carane, thujane, pinane, fenchane, *iso*-bornylane and *cyclofenchene* are mixed with carbon dioxide and passed over platinum catalyst at temperatures of 300° to 360° at atmospheric pressure. Pinane yields *p*-cymene. [Zelinski and Levina, *Ann.*, 1929, 476, 60-70.] During hydrogenation of nopinene with excess hydrogen there is isomerization of β - to α -pinene and production of *p*-cymene. [Lipp and Witgert, *Ber.*, 1930, 63B, 411-6; *Brit. Chem. Abst.*, 1930, 610A; *Chem. Abst.*, 1930, 3002.]

6309. Noble-Metal Catalysts. According to Pennycuik [*Kolloid-Z.*, 1929, **49**, 407-12; *Chem. Abst.*, 1930, 1009] part of the surface of colloidal platinum particles is probably platonic acid, the hydrogen ion of which is exchangeable for the cations of added salts. The surface ionization stabilizes the particle and gives it its negative charge. Part of the surface also contains a weakly acidic oxide of platinum which is converted by bases into an ionizing salt. This accounts for the protective action of univalent bases on colloidal platinum and for the reprecipitation of the coagulum by such bases. A platinum-iridium alloy containing 30 per cent iridium is catalytically the most active of these alloys for the carbon dioxide-hydrogen reaction, but the activity cannot be correlated with the composition because a 5 per cent alloy is more active than either a 10 or 15 per cent alloy. [Srikantan, *J. Indian Chem. Soc.*, 1929, **6**, 949-58; *Brit. Chem. Abst.*, 1930, 551A.] G. B. Taylor, Kistiakowsky, and Perry have shown that in a series of platinum-black catalysts, the preparations possessing the smaller ultimate particle size show greater catalytic activity. [*J. Phys. Chem.*, 1930, **34**, 748-52; *Brit. Chem. Abst.*, 1930, 552A.; *Chem. Abst.*, 1930, 2663.] Vrabely [*Magyar Chem. Folyóirat*, 1929, **35**, 28-32, 38-43; *Chem. Abst.*, 1929, 5398], gives a summary of the literature and a critical description of methods of catalytic hydrogenation, i.e., reduction with platinum black and hydrogen. Bourguet and Gredy postulate the preliminary formation of a complex, Pd_nH_2 , when colloidal palladium is used. They consider this complex as the actual catalyzing agent. [*Compt. rend.*, 1929, **189**, 909-11; *Brit. Chem. Abst.*, 1930, 171A.] Absorption of hydrogen by aqueous solutions of permanganate is considerably accelerated in presence of silver salts. [Hein and Daniel, *Z. anorg. Chem.*, 1929, **181**, 78-82; *Brit. Chem. Abst.*, 1929, 1020A.] X-ray investigation of palladium-silver-hydrogen alloy. [Osawa, *J. Study Met.*, 1928, **5**, 443-54; *Brit. Chem. Abst.*, 1929, 1374A.] Osmium as hydrogenation catalyst. [Zelinski and Turova-Pollak, *Ber.*, 1929, **62B**, 2865-9; *Brit. Chem. Abst.*, 1930, 77A.]

6310. Catalyst Supports. Holmes and Williams have described a method for the uniform distribution of catalysts throughout porous solids. Porous silica gel was soaked in a salt solution, and dried. A water-soluble gas was then admitted to the gel, which was later immersed in water to allow the salt and the gas to react within the capillary pores. Pairs used were: silver nitrate and hydrogen sulphide; ferric chloride and ammonia. Platinum and palladium were deposited similarly. [*Colloid Symposium Monograph*, 1928, **6**, 283-5; *Chem. Abst.*, 1929, 3844.] Impregnating porous gels with metals or other insoluble material. [Holmes, U. S. Pats. 1,739,306 and -7, Dec. 10, 1929; *Chem. Abst.*, 1930, 931.] Catalytic reactions with suspended catalysts, such as pulverized silica gel carrying active material. [Brit. Pat. 304,269, July 12, 1927, Silica Gel Corp.; *Chem. Abst.*, 1929, 4756.] Catalytic hydrogenation of organic compounds with the aid of a silicious or non-silicious base-exchange material carrying the effective catalyst. [Jaeger, Brit. Pat. 306,803, Feb. 25, 1928, to Selden Co.; *Brit. Chem. Abst.*, 1929, 806B; *Chem. Abst.*, 1929, 5192.] Catalyst masses are prepared by using a granulated carrier, for example, magnesia or lime, as a precipitant for the oxide or hydroxide of the catalyst metal. [Brit. Pat. 305,198, Dec. 3, 1928, to Holzverkohlungs-Ind. A.-G.; *Brit. Chem. Abst.*, 1930, 452B. See also French Pat. 667,784, Jan. 19, 1929; *Chem. Abst.*, 1930, 1118.] Catalysts such as chromium oxide, molybdic acid or tungstic acid or sulphides, carbides, or solid metalloids, are converted into a stable, coherent form by adding a small quantity of metals of the second or third groups such as zinc, aluminum, beryllium, cadmium, or the earth metals, or their alloys or carbides. [I. G. Farbenind. A.-G., Brit. Pat. 326,580, Dec. 24, 1928; *Chem. Age (London)*, 1930, 468; *Brit. Chem. Abst.*, 1930, 493B.]

6311. Activity of Catalyst Carriers. Adadurov and Brodovitch [*Ukraine Chem. J.*, 1929, **4**, 123-127; *Brit. Chem. Abst.*, 1929, 1245A] have investigated a number of substances used as to their own catalytic effect. Asbestos had a catalytic effect of 47 per cent, silica gel precipitated by nickelous chloride had an activity of 67 per cent, the substance precipitated by ferrous chloride 64 per cent, while refractory material itself had an activity of 73 per cent. When moistened with a mixture of 3 volumes of alum-

inum sulphate and 1 volume of chromium sulphate it had an activity of between 91.4 per cent and 100 per cent. Experiments on the hydrogenation of fumaric acid with palladium supported on blood charcoal, sugar charcoal and barium sulphate indicate that the support affects the activity of the catalyst. Of the supports tested, blood charcoal proved the most effective. [Sabalitschka and Zimmermann, *Ber.*, 1930, **63B**, 375-80; *Chem. Abst.*, 1930, 2367.]

6312. Metallic Nickel. The conditions of formation and properties of very thin electrolytic nickel deposits have been determined by Oesterle [*Z. Elektrochem.*, 1929, **35**, 505-19; *Chem. Abst.*, 1929, 5391.] Films of nickel deposited on rock salt by sputtering show a hexagonal structure on removal from the rock salt and examination by cathode ray diffraction. [Thomson, *Nature*, 1929, **123**, 912; *Chem. Abst.*, 1929, 4386.] Gas content, crystal structure, and hydrogen absorption of sputtered nickel films. [Ingersoll and Hanawalt, *Phys. Rev.*, 1929, ii, **34**, 972-7; *Brit. Chem. Abst.*, 1929, 1368A.] The lattice structure of nickel. [Valentiner and Becker, *Naturwissenschaften*, 1929, **17**, 639-40; *Chem. Abst.*, 1929, 5369.] The permeability of hot nickel to hydrogen. [Hendricks and Ralston, *J. Am. Chem. Soc.*, 1929, **51**, 3278.]

6313. Nickel Catalysts. Kusama and Uno have prepared a basic carbonate from nickel chloride and sodium carbonate. The reduced nickel is found to have the same catalytic effect as a catalyst prepared from nickel nitrate. [*Bull. Inst. Phys. Chem. Research* (Japan), 1929, **8**, 461-6; *Chem. Abst.*, 1929, 4616.] Weinberg describes the purification of solutions of nickel sulphate. [*Masloboino Zhirov. Delo*, 1928, **3**, 13-6; *Chim. et ind.*, **22**, 560-1; *Chem. Abst.*, 1930, 692.] Finely divided nickel is obtained by precipitating nickel hydroxide from a nickel salt under conditions such that the whole of the nickel is precipitated, and reducing the hydroxide. [Brit. Pat. 314,944, July 5, 1928, to N. V. de Bataafsche Petroleum Maatschappij, *Chem. Abst.*, 1930, 1476.] Finely divided copper, nickel, or cobalt is obtained by reducing the corresponding carbonate or hydroxide precipitated on kieselguhr. [Brit. Pat. 293,749, June 28, 1928, to the I. G., *Brit. Chem. Abst.*, 1929, 821B.] Weichselfelder and Kossodo describe the preparation of nickel hydride. [*Ber.*, 1929, **62B**, 769-71; *Chem. Abst.*, 1929, 4632.] Nickel carbide has been proposed as a catalyst. [H. A. Bahr and T. Bahr, *Ber.*, 1930, **63B**, 99-102; *Brit. Chem. Abst.*, 1930, 309A.] Molten material such as an alloy of iron, nickel and cobalt is cast in water to solidify it and produce a fine-grained crystalline structure; the resulting product is then reduced to finely divided condition. [Harris, to Bell Telephone Laboratories, Inc., U. S. Pat. 1,739,068, Dec. 10, 1929; *Chem. Abst.*, 1930, 820.] Martini, *Mikrochem.*, 1929, **7**, 235, reports the natural occurrence of nickel in bones. Bertrand and Mokragatz describe the distribution of nickel and cobalt in plants. They suggest that these metals may act as catalysts in vegetable cells. [*Bull. Soc. Chim.*, 1930, iv, **47**, 326-31; *Brit. Chem. Abst.*, 1930, 823A.] Rosenthaler states that nickel occurs in minute quantities in a relatively large number of drugs. [*Pharm. Zentralhalle*, 1930, **71**, 241-2; *Chem. Abst.*, 1930, 3321.] The action of nickel on hydrocarbons, halogenated in the side chain, is similar to that of copper, but a higher temperature is required. Nickel cyanide can replace cuprous cyanide in catalytic reactions between aromatic hydrocarbons and potassium cyanide. Nickel can also serve as a catalyst in the bromination of benzene, nitrobenzene and naphthalene in the same way that iron is used. [Korczynski, Reinholz and Schmidt, *Roczniki Chem.*, **9**, 731-40, 1929; *Chem. Abst.*, 1930, 1818.] Reactivated nickel does not lose its activity when kept in contact with air for one month, provided it is treated with carbon dioxide directly after exposure to hydrogen. [Bag, *Masloboino-Zhirovoe Delo*, 1928, No. 5, 6; *Chem. Abst.*, 1929, 4839.] Kazarnovski gives a survey of some methods for the regeneration of nickel from nickel catalysts freed from oil by means of extraction or saponification. [*Ibid.*, 1928, No. 1, 12-4; *Chem. Zentr.*, 1929, II, 2417; *Chem. Abst.*, 1929, 4839.] Kaluzhin reviews the losses of nickel in hydrogenation plants and considers means of minimizing them. [*Ibid.*, 1929, **45**, 10-3; *Chem. Abst.*, 1930, 2625.]

6314. Metal Carbonyls. The best results in the preparation of nickel carbonyl depend upon having very finely divided nickel. Traces of air hinder the formation of

carbonyl. Increase of pressure favors the production of iron pentacarbonyl, $\text{Fe}(\text{CO})_5$. By subjecting iron pentacarbonyl to the action of light of short wave length a diironnonacarbonyl, $\text{Fe}_2(\text{CO})_9$, results, which can be converted back to the pentacarbonyl by heating. Cobalt carbonyl, $\text{Co}(\text{CO})_4$, requires pressures of at least 30–40 atmospheres for its formation. By heating above the melting point a tricarbonyl, $\text{Co}(\text{CO})_3$, is produced. Molybdenum carbonyl, $\text{Mo}_2(\text{CO})_{10}$, is not formed at pressures less than 150 atmospheres. A chief difficulty is to get the molybdenum into an active form. The insolubility of the carbonyl in most organic solvents distinguishes it from the other carbonyls. Chromium carbonyl, $\text{Cr}(\text{CO})_6$, could not be isolated. [Mond, *Chim. et ind.*, Apr.-May, 1929; *Brenn.-Chem.*, 1929, 352.] By the action of xylene solutions of nickel carbonyl on organic compounds containing a labile halogen atom substances of high melting point are produced. The nickel of the carbonyl molecule is probably substituted by an organic group. [Gallas and Alonso, *Anal. Fis. Quim.*, 1929, 27, 663–667; *Brit. Chem. Abst.*, 1930, 80A.] In effecting reaction between cobalt and carbon monoxide, oxidizing agents such as oxygen, carbon dioxide or water vapor are excluded both from the reducing gas used in preparing the metal and from the carbon monoxide. [I. G. Farbenind. A.-G., Brit. Pat. 307,112, Dec. 3, 1927; *Chem. Abst.*, 1929, 5281.] Cobalt carbonyl obtained by the action of carbon monoxide under pressure on cobalt is separated from the reaction gases by cooling before expansion. [B.A.S.F., French Pat. 33,951, Aug. 1, 1927; *Chem. Abst.*, 1929, 4783.] The hydrogen and carbon monoxide content of some metals melted in a vacuum. [Villachon and Chaudron, *Compt. rend.*, 1929, 189, 524–6; *Chem. Abst.*, 1929, 5073.] Nickel carbonyl and acetyl chloride. [Reihlen, Gruhl and von Hessling, *Ann.*, 1929, 472, 268; *Chem. Abst.*, 1929, 4674.] Mond gives a very complete account of the metal carbonyls. [*J. Soc. Chem. Ind.*, 1930, 271T.]

6315. Manufacture of Metal Carbonyls. In order to prepare metals in the most suitable condition for production of metal carbonyls, metal oxides such as roasted pyrites or oxidic ores, are reduced by heating above 500° in the presence of hydrogen, carbon monoxide, hydrocarbons, etc., and, to prevent sintering, the metals, as soon as reduction is complete, are cooled rapidly in a non-carbonizing atmosphere preferably consisting of or containing hydrogen. [Brit. Pat. 424,382, Sept. 12, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abst.*, 1930, 289B.] Sintering of the metals during reduction may also be prevented by the presence of oxides, nitrates, carbonates, sulphates, sulphides, acetates, etc., of alkali, alkaline earth or earth metals, or the residues left in the reduced metal when the reduction is effected with lignite, semi-coke, oil shale, asphalt, and pitchlike residues. [I. G. Farbenind. A.-G., Brit. Pat. 323,021, Aug. 18, 1928; *Chem. Age* (London), 1930, 181; *Chem. Abst.*, 1930, 2841. See also French Pat. 674,216, May 2, 1929; *Chem. Abst.*, 1930, 2841.] Better yields are obtained when the materials which are to be treated with carbon monoxide are subjected to preliminary repeated oxidation and reduction. [Ger. Pat. 490,415, May 15, 1927, to the I. G., Schlecht and Kennecke, inventors; *Chem. Abst.*, 1930, 2250.] The easily fusible or slag-forming substances are removed from the ores prior to conversion by carbon monoxide. [Brit. Pat. 312,629, May 29, 1928, to the I. G.; *Chem. Abst.*, 1930, 925.] Carbon monoxide is allowed to act on metals suspended in a liquid or melt. Suitable liquids are hydrocarbons or the metal carbonyls themselves. [Brit. Pat. 323,332, Nov. 30, 1928, to the I. G.; *Brit. Chem. Abst.*, 1930, 189B.] Carbon disulphide or a sulphide of an alkali or alkaline-earth metal may be added to prevent decomposition of the carbon monoxide. [Brit. Pat. 327,956, Dec. 14, 1928, to the I. G.; *Chem. Age* (London), 1930, 581; *Brit. Chem. Abst.*, 1930, 612B.]

6316. Iron Carbonyl. The original Mond and Langer process of making iron carbonyl was very tedious and gave a yield of about 1 per cent, calculated upon the iron used. A recent I. G. Farbenind. A.-G. process uses iron ore and carbon monoxide from producer gas or water-gas, with at least 5 per cent hydrogen present, with temperatures near 500° and pressure near 200 atmospheres. It has not been possible to make the process continuous, but the gas is circulated until its carbon monoxide content is less

than 10 per cent. The iron carbonyl formed may be converted into metallic iron or oxide of great purity, suitable for use as catalyst. [Pincass, *Chem.-Ztg.*, **1929**, 53, 525-6; *Chem. Abst.*, **1929**, 4538.] Iron carbonyl is prepared by leading carbon monoxide over iron at ordinary or slightly raised pressure, and temperatures of 15°-100°. The velocity of the carbon monoxide stream is increased so as to lead off the iron carbonyl. [I. G. Farbenind. A.-G., Mittasch, Müller and Schlecht, inventors, Ger. Pat. 485,886, Mar. 31, 1925; addn. to 447,130; *Chem. Abst.*, **1930**, 1187.] Technical iron carbonyl is purified by distillation in the presence of one or more liquids which boil below 100°, such as benzol, alcohols and ketones. [Ger. Pat. 491,855, Nov. 10, 1925, to Chem. Fab. von Heyden A.-G.; Buchheim, inventor; *Chem. Abst.*, **1930**, 2555.] Coal gas stored at 50 to 80 atmospheres, has been found after 30 years to contain considerable quantities of iron pentacarbonyl. A steel cylinder was used. [Friend and Vallance, *J. Chem. Soc.*, **1930**, 718-20; *Brit. Chem. Abst.*, **1930**, 724A.] Hieber, Sonnekalb and Becker have prepared compounds of iron pentacarbonyl and various organic bases. [*Ber.*, **1930**, 63B, 973-86; *Brit. Chem. Abst.*, **1930**, 723A.] The method of preparation of iron carbonyls containing pyridine is to be stricken from the literature, since it is based upon an incorrect gas analysis. [Hieber and Sonnekalb, *Ber.*, **1929**, 62B, 422; *Chem. Abst.*, **1929**, 4449.] The reaction of carbon monoxide on iron is accelerated by the presence of metallic copper. Copper oxide may be added to iron oxide before its reduction to iron. [Vereinigte Stahlwerke Akt.-Ges., Brit. Pat. 319,356, Sept. 21, 1928; *Chem. Age* (London), **1929**, 533.] Reaction of iron carbonyl on mercaptans and also on acetyl acetone while exposed to ultraviolet rays. [Reihlen, Gruhl and von Hessling, *Ann.*, **1929**, 472, 268; *Chem. Abst.*, **1929**, 4674.] Iron carbonyl is removed from the gases used in the methanol synthesis by passing them through a layer of active carbon. [Pier, Müller-Cunradi, Wietzel and Winkler, U. S. Pat. 1,766,763, June 24, 1930, to the I. G.] The photochemical decomposition of iron carbonyl. [Eyber, *Z. physikal. Chem.*, **1929**, 144, 1-21; *Brit. Chem. Abst.*, **1929**, 1248A.] The vapor pressure and heat of vaporization of iron pentacarbonyl. [Trautz and Badstübner, *Z. Elektrochem.*, **1929**, 35, 799-802; *Brit. Chem. Abst.*, **1929**, 1372A.] The interaction of nitric oxide and iron pentacarbonyl at room temperature in the presence of methanol results in the formation of a methanol compound of iron nitrosyl. [Manchot and Gall, *Ann.*, **1929**, 470, 271-4; *Chem. Abst.*, **1929**, 3870.] Finzel outlines the best methods for preparing pyrophoric iron. [*J. Am. Chem. Soc.*, **1930**, 52, 142-9; *Chem. Abst.*, **1930**, 1275.]

6317. Iron Carbonyl in Motor Fuels. Among the substances which have been tested as anti-knocks, only lead tetraethyl and iron carbonyl appear to have found commercial application; the latter seems to be restricted to Germany, as "motyl" dope and "motalin" petrol, and it has the disadvantage that a deposit of iron oxide on the spark plugs causes short-circuiting. Nickel carbonyl and thallium oleate each have practical disadvantages, iodine compounds are costly, while aniline and its derivatives are responsible for gumming. [*J. Soc. Chem. Ind.*, **1930**, 90.] It is recommended to use in conjunction with iron carbonyl one or more organic compounds of metals or metalloids such as boron, silicon, phosphorus, etc., which are soluble in the liquid. This prevents deposition of iron oxide in the motor. [I. G. Farbenind. A.-G., Brit. Pat. 252,018; April 7, 1927.] Various organic compounds containing oxygen or nitrogen which are benzine-soluble may also be used in a liquid fuel that contains more than 0.2 gram iron carbonyl per gallon, in order to improve the anti-knock qualities imparted by the iron carbonyl and prevent oxide deposition in the motor. [I. G. Farbenind. A.-G., Brit. Pat. 252,019; March 17, 1927.] Iron carbonyl may be used in conjunction with an organic halogen compound such as a halomethane or halobenzol. [Ger. Pat. 491,431, April 5, 1925, to the I. G., addn. to 448,620; *Chem. Abst.*, **1930**, 2285.] Iron carbonyl also may be used along with lead tetraethyl or nickel carbonyl. [Hurley, Brit. Pat. 315,706, July 16, 1928; *Chem. Abst.*, **1930**, 1735.]

6318. Uses of Metal Carbonyls. Hydrocarbons, mainly liquid, are produced by the thermal decomposition of metal carbonyls in the presence of hydrogen. [I. G. Farbenind. A.-G., Ger. Pat. 487,379, May 11, 1926, Müller, Schlecht and Schubardt, inventors;

Chem. Abst., 1930, 2139.] Metallic deposits are produced from carbonyls by introducing them into a vessel in which the article to be coated is maintained at a temperature above that of the decomposition of the carbonyl. If the deposit is made on a soluble substance, such as a large crystal of sylvine, a thin transparent film of the metal is obtained by subsequent dissolution of this substance. [Brit. Pat. 324,363, Oct. 12, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abst.*, 1930, 289B.] Finely divided iron produced by the thermal decomposition of iron carbonyl is formed into magnet cores by molding under pressure with a binder consisting of a urea-formaldehyde resin. [Brit. Pat. 319,854, July 14, 1928, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1930, 2847.] Montan wax or conversion products of the wax may also be used as a binder. [Brit. Pat. 320,016, *Chem. Abst.*, 1930, 2847.] Metal powders may be mixed with pitches and asphalts to form magnet cores. A soft coumaron resin may be added to the pitch if desired. [Brit. Pat. 320,611, July 14, 1928; *Chem. Abst.*, 1930, 2847.] Wittek recommends the use of metal carbonyls or their metallic decomposition products as plant stimulants. They may be applied to the soil or to seeds, and may also be used alone or mixed with fertilizers. [Ger. Pat. 493,367, Nov. 24, 1928; *Chem. Abst.*, 1930, 2827.] Insulating masses are produced by passing jets of iron or nickel carbonyl into melted paraffin. The carbonyl is decomposed and finely divided metal remains suspended in the paraffin. [Siemens & Halske A.-G., Brit. Pat. 306,900, Feb. 19, 1928; *Brit. Chem. Abst.*, 1930, 429B; *Chem. Abst.*, 1929, 5254.] Organic insulators such as those used for condenser foils, which are unstable at slightly raised temperatures, are coated with metal by deposition from the vapor of iron or nickel carbonyl. [Siemens & Halske A.-G., Brit. Pat. 306,902, Feb. 27, 1928; *Chem. Abst.*, 1929, 5255.]

6319. Dehydrogenation. Zelinski and Balandin [*Bull. acad. sci. union rep. sov. social., Classe sci. phys.-math.*, 1929, 29-52; *Chem. Abst.*, 1930, 774] have made a quantitative study of the catalytic dehydrogenation of decahydronaphthalene: $C_{10}H_{18} = C_{10}H_8 + 5H_2$. Platinized active charcoal is three and one-half times as effective in this catalysis as platinum deposited on asbestos. Arrhenius' formula, $k = k_0 e^{-Q/RT}$, applies up to 270°. Above 270° the catalyzing surface begins to destroy decahydronaphthalene and, on becoming covered with a thin film of the decomposition products, gradually loses its activity. $\alpha\gamma$ -Diphenylpropane is unchanged by passage over platinized charcoal at 300°-310° in an atmosphere of carbon dioxide. Stilbene at 300° affords phenanthrene quantitatively. Hydrindane gives a mixture of unchanged material and hydrindene. $\alpha\beta$ -Dicyclohexylethane is dehydrogenated successively to dibenzyl, 9:10-dihydrophenanthrene, and phenanthrene. [Zelinski and Titz, *Ber.*, 1929, 62B, 2869-2873; *Brit. Chem. Abst.*, 1930, 80A.] Mixtures of basic and acidic oxides (with the latter in excess) are used for dehydrogenation, prepared by igniting compounds such as basic zinc ammonium chromate, with or without small additions of alkali metal compounds. [Lazier and Zeisberg (to E. I. DuPont de Nemours & Co.), Brit. Pat. 313,093, June 6, 1928; *Chem. Abst.*, 1930, 860.] Dehydrogenation reactions such as the conversion of ethyl alcohol into ethyl acetate are effected at high temperatures and pressures with a catalyst comprising copper and one or more difficultly reducible oxides such as those of metals of the second group. [Lazier (to E. I. DuPont de Nemours & Co.), Brit. Pat. 312,345, May 26, 1928; *Chem. Abst.*, 1930, 862.]

6320. Exchange Hydrogenation. By treating a compound which is capable of splitting off hydrogen with one capable of easy reduction, in presence of an activating agent (palladium-black), transference of hydrogen takes place from the former to the latter. Cinnamic acid, oleic acid, eugenol, and coumarin when heated with tetrahydronaphthalene and palladium give good yields of hydrocinnamic acid, stearic acid, hydroeugenol, and hydrocoumarin, respectively. A mixture of tetrahydroquinoline (1 mol) and maleic acid (2 mols) is converted quantitatively into quinoline and succinic acid. Piperidine is not reduced by maleic acid and palladium but gives an almost theoretical yield of pyridine with saffrole and palladium. Tetrahydroisoquinoline is, and tetrahydropapaverine is not, reduced by anethole and palladium; nicotine gives small quantities of nicotyrine with these reagents. [Akabori and Suzuki, *Proc. Imp. Acad. Tokyo*,

1929, 5, 255-6; *Brit. Chem. Abst.*, 1929, 1170A.] A "more or less completely hydrogenated compound" is caused to react with a compound capable of taking up hydrogen, in the presence of a hydrogenation catalyst or catalyst mixture. Cyclohexanone is formed from cyclohexanol and phenol. Camphor is formed from isoborneol and phenol, or from isoborneol and carbon monoxide under pressure. [Schering-Kahlbaum A.-G., *Brit. Pat.* 310,055, April 21, 1928; *Chem. Abst.*, 1930, 625. See also French Pat. 672,780, April 6, 1929.]

6321. Competitive Hydrogenation. The factors determining the distribution of hydrogen by platinum between two competing reactants bear little relationship to those factors which determine the amount of material reacting in unit time. The addition of zinc and nickel acetates retards the rate of reduction but does not modify the distribution of hydrogen. It seems that the salts poison the catalyst for the reaction of the two unsaturated compounds to an equal extent, presumably through adsorption in certain areas of the catalyst. It may be suspected that in addition to this the solvent plays a part in the rate of formation and the stability of an intermediate compound of platinum-hydrogen-reactant-solvent. The relative ease of reduction of two substances in a mixture may not be certainly determined even qualitatively by determining the rates of reduction of the two substances separately. [Adkins, Diwoky and Broderick, *J. Am. Chem. Soc.*, 1929, 51, 3418-23; *Chem. Abst.*, 1930, 94.]

6322. Hydrogenation in Analysis. The catalytic hydrogenation of mixtures of pinene and dipentene proved to be a satisfactory method of determining the proportion of the two constituents. Pinene absorbs one mole of hydrogen, dipentene two; the two compounds are isomeric; therefore the composition of a mixture may be calculated from the amount of hydrogen absorbed by a given weight of material. [Conant and Carlson, *J. Amer. Chem. Soc.*, 1929, 51, 3465.] The hydrogenation of supposedly pure cyclohexene yielded some water, thus showing the presence of an impurity containing oxygen. [Waterman and van Westen, *Rec. trav. chim.*, 1929, 48, 637-9; *Chem. Abst.*, 1929, 4455.] Shaefer describes a simple and accurate method for quantitative hydrogenation at ordinary temperature and atmospheric pressure with palladium as a catalyst. The method was used in the hydrogenation of maleic acid, α -terpineol, abietic acid and ethyl abietate. It is stated that the method should prove of value in the study of pure compounds of unknown constitution. [*Ind. and Eng. Chem., Analyt. Edit.*, 1930, 2, 115.] Opotzki [*J. Chem. Ind. (Russia)*, 1929, 6, 532-3; *Chem. Abst.*, 1930, 803] gives a review of ter Meulen's work on the determination of oxygen, nitrogen, sulphur, chlorine, bromine, arsenic and mercury in organic compounds by hydrogenation. When the quantity of halogen fixed by the action of halogenating reagents on ethylene compounds is less than the theoretical iodine number, Cerdeiras suggests that it should be compared with the hydrogen value. [*Anales soc. españ. fis. quim.*, 1930, 28, 56-62; *Chem. Abst.*, 1930, 2000.] "Subsidiary odors" are destroyed by selective hydrogenation of impurities present in resins, balsams, essential oils or synthetic products such as ionone or methyl ionone. [I. G. Farbenind. A.-G., *Brit. Pat.* 305,555, Oct. 29, 1927; *Chem. Abst.*, 1929, 4778.] Hydrogenation is sometimes an aid in the identification of organic substances. For example, Walbaum and Rosenthal [*Ber. Schimmel*, 1929, 209-218; *Brit. Chem. Abst.*, 1929, 1049B], obtained an oil from the French violet which by fractional distillation yielded an aldehyde and this was oxidized to the corresponding acid and then converted into the methyl ester. When the latter compound was reduced by palladium and hydrogen, with the resulting addition of 4 atoms of hydrogen, methyl nonoate was produced. Analysis of *d*- β -octyl *p*-dimethylaminobenzoate has been effected by ter Meulen's method, nickel being used as the catalyst. [Rule, Miles and MacGillivray, *J. Chem. Soc.*, 1929, 2279.] A method for the determination of the hydrogen value of unsaturated compounds is described by Waterman, Perquin and van Westen. Hydrogenation is performed in the presence of a catalyst, and the volume of gas absorbed is measured directly. [*J. Soc. Chem. Ind.*, 1928, 47, 363-5T; *Chem. Abst.*, 1929, 5079.] Preparation of substances showing a theoretical hydrogen value: amylene [Waterman, van't Spijker and van Westen, *Rec. trav. chim.*, 1929, 48, 612-5; *Chem. Abst.*, 1929,

4439], hexadecene [*Idem, ibid.*, 1103-11; *Chem. Abst.*, 1930, 823], decylene [*Idem, ibid.*, 1097-102; *Chem. Abst.*, 1930, 823], pinene [*Idem, ibid.*, 1191-8; *Chem. Abst.*, 1930, 824], isoprene [Waterman and van Westen, *ibid.*, 1084-6; *Chem. Abst.*, 1930, 824.]

6323. Hydrocarbons. Heated to 1000°-1100° C. for one-fifth to one-twentieth of a second, methane gives benzene and other aromatic hydrocarbons. Hydrogen is also formed and may be reconverted to methane by reaction with carbon monoxide or dioxide, using a nickel catalyst. [Fischer and Pichler, *Brit. Pat.* 316,126, July 23, 1928; *Chem. Age* (London), 1929, 294; *Chem. Abst.*, 1930, 1649.] Aromatic hydrocarbons are obtained by passing methane or ethane together with unsaturated hydrocarbons over catalysts. [Brit. Pat. 311,899, April 10, 1928; *Chem. Abst.*, 1930, 860.] Hydrogen is removed from the residual gases by passing them over cupric oxide, by diffusion, or by treatment with carbon monoxide and nickel. [Wheeler, *Brit. Pat.* 324,939, Sept. 3, 1928, to Imperial Chem. Industries, Ltd.; *Brit. Chem. Abst.*, 1930, 406B.] To produce acetylene and hydrogen from saturated hydrocarbons, the gases are passed through several arcs. [I. G. Farbenind. A.-G., French Pat. 674,459, May 2, 1929; *Chem. Abst.*, 1930, 2385.] Taylor and Hill [*J. Amer. Chem. Soc.*, 1929, 51, 2922-36] have made a study of the reaction between hydrogen and ethylene under the influence of excited mercury atoms and with varying conditions of pressure, concentration and temperature. Pease has studied the non-catalytic polymerization and hydrogenation of pure ethylene. [*J. Amer. Chem. Soc.*, 1930, 52, 1158-64; *Brit. Chem. Abst.*, 1930, 709A.] The action of hydrogen on organo-metallic lead compounds such as lead tetraphenyl, tetraethyl, and tetramethyl results in irreversible displacement of the metal and production of a hydrocarbon according to the equation: $PbR_4 + 2H_2 = Pb + 4RH$. [Ipatiev, Razubaiev and Bogdanov, *Ber.*, 1930, 63B, 335-42; *Brit. Chem. Abst.*, 1930, 463A.] The thermal decomposition of mercury diethyl in a mixture of ethylene and hydrogen has been found to produce mainly an ethylenic polymer and a small amount of saturated hydrocarbons. [Taylor and Jones, *J. Amer. Chem. Soc.*, 1930, 52, 1111-21.] Hydrogenation of pentachlorethane (nickel at 270°) yields trichlorethylene. Over nickel chloride it yields tetrachlorethylene. [Mailhe and Sabron, *Bull. Soc. chim.*, 1930, iv, 47, 349-50; *Brit. Chem. Abst.*, 1930, 735A.] Chamberlin and Bloom describe experiments dealing with the thermal decomposition of natural gas in tubes of silica, steel, copper, iron, nickel, monel and clay. Between temperatures of 500° and 900° C. the various tubes have different effects on converting methane into benzene, naphthalene, anthracene, acetylene, etc. [*Ind. & Eng. Chem.*, 1929, 21, 945.] Thermal reactions of pure organic substances with hydrogen under high pressures. [Hofmann and Long, *Brennstoff-Chem.*, 1929, 10, 203-5; *Chem. Abst.*, 1930, 596.] Behavior of various organic vapors under high-tension oscillatory discharges. [Hiedemann, *Ann. Physik*, 1929 (5), 2, 221-32; *Chem. Abst.*, 1929, 4858.] The action of the spark discharge on methane. [Stanley and Nash, *J. Soc. Chem. Ind.*, 1929, 48, 238-42T.] The splitting of organic compounds by catalytic hydrogenation and the rôle of nickel in heterogeneous catalysis. [Balandin, *Z. physik. Chem.*, Abt. B, 1929, 3, 167-94; *Chem. Abst.*, 1929, 5090.] Catalytic hydrogenation of halogenated organic compounds. [Busch and Schmidt, *Ber.*, 1929, 62B, 2612-20; *Brit. Chem. Abst.*, 1929, 1433A.] Synthesis and free energy of methane. [Randall and Mohammad, *Ind. & Eng. Chem.*, 1929, 21, 1048-52; *Brit. Chem. Abst.*, 1930, 49B.] Lush gives a review of the hydrogenation of organic compounds. [*Ind. Chemist*, 1930, 6, 142-4; *Chem. Abst.*, 1930, 2715.] Frolich, White and Dayton have studied the cracking of pure methane at temperatures above 1000° C. and pressures down to 25 mm. At these temperatures acetylene is a primary product but has a tendency to polymerize into benzene and similar compounds as well as to decompose further into carbon and hydrogen. [*Ind. Eng. Chem.*, 1930, 22, 20-3.]

6324. Ethylenic Hydrocarbons. Hydrogenation of squalene, obtained from the liver oil of *Centrophorus granulosus*. [Heilbron and Thompson, *J. Chem. Soc.*, 1929, 883.] Hydrogenation of illipene, obtained from the unsaponifiable matter of illipé butter. [Tsujiyamoto, *J. Soc. Chem. Ind. Japan*, 1929, 32, 365-7B; *Brit. Chem. Abst.*,

1930, 317A.] The catalytic reduction with platinum-black of 1-isoamyl- Δ^1 -cyclopentene affords isoamylcyclopentane. [Harris, *J. Amer. Chem. Soc.*, 1929, **51**, 2591; *Brit. Chem. Abst.*, 1929, 1170A.] Hydrogenation of 2,3,6,7-tetramethyl-2,6-octadiene gives 2,3,6,7-tetramethyloctane. [Midgley and Henne, *J. Am. Chem. Soc.*, 1930, **52**, 2077-8; *Chem. Abst.*, 1930, 3129.] Synthesis of 1,2-dimethyl-3-isopropylcyclopentane by catalytic reactions. [Kasanski, *Ber.*, 1929, **62B**, 2205-10; *Chem. Abst.*, 1930, 75.] Cyclic disubstituted ethylenic derivatives are hydrogenated more readily than trisubstituted ones and the latter more readily than tetrasubstituted ones. [Lebedev and Platonov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2151-74, and *J. Chem. Soc.*, 1930, 321-36; *Brit. Chem. Abst.*, 1930, 587A; *Chem. Abst.*, 1930, 2729.] Δ^1 -Cyclohexylcyclohexene is reduced catalytically (palladized charcoal) to dicyclohexyl. [Hückel, Neunhoeffer, Gercke and Frank, *Ann.*, 1929, **477**, 99-160; *Brit. Chem. Abst.*, 1930, 206A.] Beaucourt describes the hydrogenation of a hydrocarbon obtained by distillation of boswellic acid from olibanum. [*Monatsh.*, 1929, **53** and **54**, 897-913; *Brit. Chem. Abst.*, 1929, 1457A.]

6325. Unsaturated Alcohols and Amines. 2-Octene-4-ol is reduced with hydrogen and palladium to give octane-4-ol. 1-Heptene-3-ol on reduction gives heptane-3-ol. [Levene and Haller, *J. Biol. Chem.*, 1929, **83**, 578-89; *Brit. Chem. Abst.*, 1929, 1266A.] *l*-Hexa-1,5-diene-3-ol gives *d*-hexane-3-ol. [*Idem.*, *ibid.*, 1929, **83**, 185-90; *Brit. Chem. Abst.*, 1929, 1041A.] *d*-Methylheptenol, gives *d*-2-methylheptane-6-ol. [*Idem.*, *ibid.*, 1929, **83**, 177-83; *Brit. Chem. Abst.*, 1929, 1038A.] Dibenzoyldiaminoethylene is obtained by benzylation of imidazole in alkaline solution. It is catalytically reduced in presence of palladium or nickel to give dibenzoyldiaminoethane. [Ruggli, Ratti and Henzi, *Helv. Chim. Acta*, 1929, **12**, 332-61; *Chem. Abst.*, 1930, 116.] Guyot and Fournier have used hydrogenation catalysts consisting of nickel, cobalt, copper and iron in the preparation of primary and secondary amines from alcohols and ammonia or amines. [*Bull. Soc. chim.*, 1930, **47**, 203-10; *Chem. Abst.*, 1930, 2992.] Organic bases which are valuable as insecticides are produced by acting on an aliphatic hydrocarbon containing more than one double bond with a nitrogenous base, such as ammonia or primary or secondary amines, in the presence of an alkali metal or an alloy of alkali metals. Methyl-dibutenylamine is prepared from methylamine and butadiene; methyl-dibutylamine is obtained by hydrogenation of this base in the presence of palladium; *N*-butenylpiperidine prepared by the reaction between piperidine and butadiene is catalytically reduced in presence of palladium to give *N*-butylpiperidine. [*Brit. Pat.* 313,934, Jan. 14, 1928, to I. G.] 2-*n*-Amylquinoline is prepared synthetically by condensation of 2-methylquinoline with *n*-butaldehyde to the unsaturated base, $C_{11}H_{12}N$, and hydrogenation of the latter compound in presence of palladized charcoal. [Späth and Pikl, *Ber.*, 1929, **62B**, 2244-51; *Brit. Chem. Abst.*, 1929, 1319A.] Meisenheimer and Link describe the following reductions with platinum-black: α -phenylallyl ethyl ether to α -phenyl-*n*-propyl ethyl ether; cinnamylethylaniline to γ -phenyl-*n*-propylethylaniline; phenyl- Δ^2 -pentenylmethylamine to *n*-amylmethylaniline; diethyl- Δ^2 -pentenylamine to diethyl-*n*-amylamine; α -phthalimido- Δ^2 -pentene to *n*-amylphthalimide. [*Ann.*, 1930, **479**, 211-77; *Brit. Chem. Abst.*, 1930 769A.]

6326. Unsaturated Aldehydes and Ketones. In presence of platinum-black, hydrogenation of 2-ethylidenecyclohexanone gives 2-ethylcyclohexanone, and 2-propylidenecyclohexanone gives 2-propylcyclohexanone. [Vavon and Mitchovitch, *Bull. Soc. chim.*, 1929, iv, **45**, 961-72; *Brit. Chem. Abst.*, 1930, 206A.] Reduction of cinnamaldehyde in presence of alcohol and alumina gives β -phenylpropionaldehyde. [Weston and Adkins, *J. Am. Chem. Soc.*, 1929, **51**, 2589; *Chem. Abst.*, 1929, 4461.] 1,3-Dipropylidenecyclopentan-2-one, hydrogenated in ether in presence of platinum-black, is converted into *cis*-1,3-dipropylcyclopentan-2-one. Reduction of the latter in acetic acid affords mainly *cis*-1,3-dipropyl-*cis-cis*-cyclopentan-2-ol. [Vavon and Flurer, *Bull. Soc. chim.*, 1929, (iv), **45**, 763-7; *Brit. Chem. Abst.*, 1929, 1299A.] 5-Benzylidene-2-methylcyclopentanone gives 5-benzyl-2-methylcyclopentanone. 2-Methyl-5-isopropylidenecyclopentanone gives 2-methyl-5-isopropylcyclopentanone. [Cornubert and Borrel, *Bull. Soc. chim.*, 1930, iv, **47**, 301-22; *Brit. Chem. Abst.*, 1930, 776A.] Dibenzylidene-

cyclopentylidenecyclopentanone is hydrogenated in presence of nickel to give the dibenzyl compound. [Cornubert, *Compt. rend.*, 1930, **190**, 440-2; *Brit. Chem. Abst.*, **1930**, 474A; *Chem. Abst.*, **1930**, 3225.] 1-Propylcyclopentan-2-one is obtained by hydrogenation of 1-propylidenecyclopentan-2-one in ether in presence of platinum-black. [Vavon and Flurer, *Bull. Soc. chim.*, 1929, (iv), **45**, 754; *Brit. Chem. Abst.*, **1929**, 1290A.] 2-Benzyl-6-methylcyclohexanone, obtained by catalytic hydrogenation of benzylidene-2-methylcyclohexanone in presence of platinum or nickel. [Cornubert and Borrel, *Bull. Soc. chim.*, 1929, iv, **45**, 1148-61; *Brit. Chem. Abst.*, **1930**, 347A; *Chem. Abst.*, **1930**, 2730.] 2-Methylstyryl ethyl ketone, on hydrogenation in presence of colloidal palladium, gives β - α -tolyl-diethyl ketone. [Harvey, Heilbron and Wilkinson, *J. Chem. Soc.*, **1929**, 425; *Brit. Chem. Abst.*, **1930**, 593A.] When the phenylhydrazine of α -hydroxydiphenylacetaldehyde is boiled with dilute sulphuric acid it loses 1 mol of water and forms a red substance which is probably diphenylketenphenylhydrazone. When the latter is reduced by hydrogen in presence of palladized charcoal and benzene the phenylhydrazone of diphenylacetaldehyde is obtained. [Zerner and Goldhammer, *Monatsh.*, 1929, **53** and **54**, 485-92; *Brit. Chem. Abst.*, **1929**, 1450A.]

6327. Unsaturated Acids and Esters. Succinic esters are prepared by hydrogenating a mixture of fumaric or maleic acid and an alcohol at a raised temperature. Malic esters are prepared by using steam instead of hydrogen. [I. G. Farbenind. A.-G., Ger. Pat. 485,313, Nov. 8, 1924; *Chem. Abst.*, **1930**, 862.] Potassium phenyl-isopropyl, $K-C(CH_3)_2 \cdot C_6H_5$, reacts with certain unsaturated hydrocarbons by substitution of metal (usually in a methyl group) to form an organo-metallic compound of the unsaturated hydrocarbon. When this is decomposed by means of carbon dioxide an unsaturated acid is obtained. Thus, $\omega\omega$ -dimethylstyrene yields β -benzylidene-*n*-butyric acid, reduced by hydrogen in presence of palladized barium sulphate and alcohol to β -benzyl-*n*-butyric acid; $\alpha\alpha$ -diphenyl- Δ^2 -propylene gives $\gamma\gamma$ -diphenyl- Δ^2 -butenoic acid, reduced to $\gamma\gamma$ -diphenylbutyric acid; $\alpha\alpha$ -diphenyl- $\beta\beta$ -dimethylethylene affords an acid, reduced to β -benzhydryl-*n*-butyric acid. [Ziegler, Crössman, Kleiner and Schäfer, *Ann.*, 1929, **473**, 1-35; *Brit. Chem. Abst.*, **1929**, 1091A.] Ethyl 2-methyl-5-allylcyclopentanone-5-carboxylate gives ethyl 2-methyl-5-propylcyclopentanone-5-carboxylate. [Cornubert and Borrel, *Bull. Soc. chim.*, 1930, iv, **47**, 301-22; *Brit. Chem. Abst.*, **1930**, 776A.] Isocrotonic acid is much more readily reduced than is crotonic acid. This confirms its *cis*-configuration, since *cis*-forms are more readily and smoothly hydrogenated than the *trans*-forms. Differences in the rates of hydrogenation of erucic and brassic acids serve to establish them as *cis*- and *trans*-varieties, respectively. [Paal and Schiedewitz, *Ber.*, 1930, **63B**, 766-78; *Brit. Chem. Abst.*, **1930**, 740A.] 3-Methyl- Δ^2 -pentenoic acid is hydrogenated to 3-methyl-valeric acid. [Reichstein, *Ber.*, 1930, **63B**, 749-54; *Brit. Chem. Abst.*, **1930**, 611A.] Benzaldehyde, malonic acid, and piperidine react to form piperidine benzylidenemalonate and not a β -amino- β -arylethane- α -dicarboxylic acid as described by Rodionov. [*Brit. Chem. Abst.*, **1929**, 557.] One proof of this is that when the compound is reduced with hydrogen and palladized barium sulphate, benzylmalonic acid is obtained. [Boehm, *Arch. Pharm.*, 1929, **267**, 702-14; *Brit. Chem. Abst.*, **1930**, 88A.] Hydrogenation of α -acetamidoacrylic acid in the presence of palladium gives acetyl-*dl*-alanine. [Bergmann and Grafe, *Z. physiol. Chem.*, 1930, **187**, 187-95; *Brit. Chem. Abst.*, **1930**, 585A.] van Romburgh and van Veen have described the hydrogenation of a highly unsaturated acid obtained from the resinous exudation from the wood of *Pentaspadon motleyi*. [*Proc. Acad. Sci. Amsterdam*, 1929, **32**, 692-7; *Chem. Abst.*, **1930**, 123.] Hydrogenation of glycyldihydrophenylalanyl-glycine yields glycyld-phenylalanyl-glycine. Glycyldihydrophenylalanyl-*d*-glutamic acid yields glycyld-phenylalanyl-*d*-glutamic acid. [Bergmann, Schmitt and Miekeley, *Z. physiol. Chem.*, 1930, **187**, 264-76; *Brit. Chem. Abst.*, **1930**, 772A.] Proteins, reduced by hydrogen and spongy palladium, give the corresponding thiol compounds. *L*-Cystine gives *L*-cysteine; dialanylcystine, dialanylcysteine. [Bergmann and Michalis, *Ber.*, 1930, **63B**, 987-9; *Brit. Chem. Abst.*, **1930**, 754A.] Ethyl β -phenyl- Δ^1 -butenoate is reduced (nickel) to ethyl α -phenylbutyrate. [Rupe and van Walraven, *Helv. Chim.*

Acta, 1930, **13**, 361-77; *Brit. Chem. Abst.*, 1930, 770A.] 3,4-Dimethoxy-6-vinylbenzoic acid, reduced (palladium) to 3,4-dimethoxy-6-ethylbenzoic acid. [H. Kondo and T. Kondo, *J. pr. Chem.*, 1930, ii, **126**, 24-52; *Brit. Chem. Abst.*, 1930, 794A.] Catalytic reduction, with hydrogen under ordinary pressure with a nickel catalyst deposited on diatomaceous earth, of pure ethyl α -eleostearate, and ethyl β -eleostearate, has been repeated and the previous results have been confirmed. [See *Brit. Chem. Abst.*, 1927, 1169A.] This presents further proof that eleostearic acid contains a conjugated system of three double bonds. [Boeseken, van Krimpen and Blanken, *Rec. trav. chim.*, 1930, **49**, 247-56; *Brit. Chem. Abst.*, 1930, 451A.] Iso-oleic acid, which is produced during the hydrogenation of oleic acid, has been found to consist of a mixture containing a considerable amount of solid Δ -9,10 oleic acid (Δ -9,10 elaidic acid?) and a small quantity of other solid oleic acids (Δ -10,11 oleic acid?; Δ -11,12 oleic acid?). The double bond of ordinary oleic acid migrates to a certain extent during hydrogenation. [Ueno and Kusel, *J. Soc. Chem. Ind., Japan*, **33**, Suppl. binding 62, 1930; *Chem. Abst.*, 1930, 2908; *Brit. Chem. Abst.*, 1930, 577A.]

6328. Hydrogenation of Marine Oils. By polymerization of fish oil in an atmosphere of hydrogen at 280°-290° for 14 hours the characteristic odor of the oil disappears, and is not regenerated by hydrolysis, heating, or keeping of the product. Strong sunlight, however, rapidly causes the products to become odorous. [Hashi, *J. Soc. Chem. Ind., Japan*, 1930, **33**, 58B; *Brit. Chem. Abst.*, 1930, 430B.] Cod-liver oil is deodorized by the silent discharge. The oil retains its vitamin and nutritive value. [Iwamoto, *ibid.*, 1929, **32**, 308-12; *Chem. Abst.*, 1929, 4840.] The physical and chemical properties of hydrogenated sardine oil, herring oil and cod-liver oil are not appreciably affected by ultraviolet irradiation. The antirachitic value of the fats is considerably increased by irradiation. [Ueno, Yamashita and Ota, *ibid.*, 1930, **33**, 61B; *Brit. Chem. Abst.*, 1930, 430B.] Suzuki and Yokoyama have isolated and hydrogenated two new acids from sardine oil. [*Proc. Imp. Acad. Tokyo*, 1929, **5**, 265-73; *Brit. Chem. Abst.*, 1929, 1271A.] Ueno has found that the catalytic activity of platinum and nickel in the hydrogenation of sardine oils is reduced by treatment with anaesthetics. [*J. Soc. Chem. Ind., Japan*, 1929, **32**, 321-3B; *Brit. Chem. Abst.*, 1930, 282B.] By hydrogenation of sperm oil over a nickel catalyst large quantities of octadecyl alcohol are obtained. [François, *Bull. Mat. Grasses*, 1929, 189-202; *Brit. Chem. Abst.*, 1929, 860B.] The precipitated semi-solid glycerides of pilchard oil have been hydrogenated to a solid white, odorless and tasteless mass. [Brocklesby, *Can. Chem. Met.*, 1929, **13**, 212-4; *Chem. Abst.*, 1929, 4585.]

6329. Hydrogenation of Other Oils. Waterman and van Tussenbroek [*Chem. Weekblad.*, 1929, **26**, 410-3; *Brit. Chem. Abst.*, 1929, 861B; *Chem. Abst.*, 1929, 5340] have conducted investigations on the effect of heating soya bean oil in air and *in vacuo*, with and without the addition of nickel. They conclude that the changes in the constants of the oil when heated with nickel arise chiefly from changes in the glycerides of linoleic acid. [*Ibid.*, 1929, **26**, 566-7; *Brit. Chem. Abst.*, 1930, 66B.] Ueno and Kuzei [*J. Soc. Chem. Ind., Japan*, 1928, **31**, 217-20; *Chem. Abst.*, 1930, 2320] have determined the comparative amounts of unsaturated solid acids (so-called iso-oleic acids) formed during the hydrogenation of soya bean oil with mixed catalysts prepared in various ways. The chrysalides of the silk-worm on extraction yield over 20 per cent. of an oil which can be readily solidified by hydrogenation. [DeConno and Quarto, *Ann. chim. applicata*, 1929, **19**, 91-7, *Chem. Abst.*, 1929, 5053; cf. Paras. 3277-9.] Markman and Vasiliev have studied the effect of temperature on the hydrogenation process of sunflower oil. [Maslob.-Zhiron. Delo, 1928, No. 8, 23-4; *Chem. Abst.*, 1929, 4839.] Slightly deteriorated linseed oil absorbs more hydrogen than can be accounted for by the decrease in iodine number. This is explained by reduction of hydroxyl groups formed during the oxidation process. [Vasiliev, *ibid.*, 1928, No. 7, 9-11; *Chem. Abst.*, 1929, 4839.] Heat-bodied drying oils, when hydrogenated, always yield stearic acid, indicating that the so-called polymerization is an extra-molecular phenomenon. [Cutter, *J. Oil and Colour Chem. Assoc.*, 1930, **13**, 66-83; *Chem. Abst.*, 1930, 2901.] An interesting method of hardening

oils and fats is described by von der Heide [Ger. Pat. 482,919, June 17, 1926; *Chem. Abst.*, 1930, 519.] Unsaturated oils and fats are hardened by adding them, generally in emulsified form, to cultures of hydrogen-producing bacteria. Hardening oils and fats. [Burman, Brit. Pat. 309,502, April 11, 1928; *Chem. Abst.*, 1930, 744.] Chogo describes an apparatus for mixing liquid and gas, which is applicable to the hydrogenation of fats. [U. S. Pat. 1,740,441, Dec. 24, 1929, to S. Kubota; *Brit. Chem. Abst.*, 1930, 538B.]

6330. Uses of Hydrogenated Oils. Soaps which contain beef tallow are less stable than those that contain "stearol" (hydrogenated fish oil), according to Tomajoti [Olie Grassi, June 30, 1929; *Brit. Soap Manufr.*, 1929, 5, 235-6.] The properties and constitution of kusum (macassar) fat from the seeds of *Schleichera trijuga*, which grows abundantly in various parts of India, have been studied by Dhingra, Hilditch and Vickery. [*J.S.C.I.*, 1929, 48, 281-286T; *Brit. Chem. Abst.*, 1929, 1022B.] The qualities of the soap are reminiscent of those of a hydrogenated fish oil. Montero describes the various uses of hydrogenated fish oil. [*Quim. e ind.*, 1930, 7, 28-9; *Chem. Abst.*, 1930, 2321.] Hydrogenated sunflower-seed oil is said to contain forty-five per cent of iso-oleic acid. It is claimed that the presence of various isomers of oleic acid in such hydrogenated sunflower oil makes the material more suitable for the manufacture of soap. [*Maslob.-Zhiron. Delo*, 1927, No. 1, 23-7; *Oil & Fat Ind.*, Oct., 1929, 37.] Astra fat is a white, soft, hydrogenated peanut oil in which the iodine number due to unsaturated acids is reduced from 95 to about 63. [Gfeller, *Pharm. Acta Helv.*, 1928, 3, 154-63; *Chem. Abst.*, 1929, 5011.] According to Maeder [*Pharm. Acta Helv.*, 1929, 4, 56-8; *Chem. Abst.*, 1929, 5011] astra fat is a suitable substitute for hog lard in pharmaceutical preparations in view of its appearance and keeping qualities. When lard is mixed with 25 per cent of hydrogenated oil it does not become rancid. [Fiero, *Am. J. Pharm.*, 1930, 102, 146-54; *Chem. Abst.*, 1930, 2318.] Freedman and Rickets describe products having piezoelectric properties and containing hydrogenated oils or fats. [Brit. Pat. 311,055, March 29, 1928; *Chem. Abst.*, 1930, 699.] The product obtained by treating a mixture of colophony and castor oil with hydrogen under pressure and at a raised temperature is used as initial material for the manufacture of greases. [A. Riebeck'sche Montanwerke A.-G., Ger. Pat. 482,965, June 23, 1922; *Chem. Abst.*, 1930, 519-20.] A viscous mass, suitable for pharmaceutical purposes, is obtained by heating castor oil and formaldehyde with a catalyst such as nickel. [Hauschka, U. S. Pat. 1,728,205, Sept. 17, 1929; *Chem. Abst.*, 1929, 5276.] Hardened blubber oil, heated with butyric acid and glycerol, is suggested as a butter substitute. [Täufel and Preiss, *Z. Unters. Lebensm.*, 1929, 58, 425-33; *Brit. Chem. Abst.*, 1930, 568B.] Smith [*Food Manuf.*, 1929, 4, 130-2, 197-8, 343-6, 367] outlines the utilization of oils and their hydrogenation products in the foodstuff industry.

6331. Analysis of Hydrogenated Oils. Kaufmann describes the detection of hardened fats by spectroscopical identification of nickel. The nickel solution obtained from cautiously ashed fat (1-50 g.), or by acid extraction, is electrolyzed, the nickel being deposited on the tip of copper-plated platinum wire electrodes, and subsequently identified by its spark spectrum. Careful manipulation is essential, but quantities down to 10^{-6} milligrams of nickel (0.0001 mg. of nickel per kg. of fat mixture) can be identified with certainty. [*Chem. Umschau*, 1930, 37, 17-21; *Brit. Chem. Abst.*, 1930, 430B.] Kubelka, Wagner and Zuravlev [*Collegium*, 1929, 374-396; *Brit. Chem. Abst.*, 1929, 924B] have made comparative determinations of the iodine values of hardened whale, rape, sesame, cod-liver, linseed, and castor oils, by the Hanus, Margosches, and Rosenmund methods. Trevithick and Lauro [*Oil & Fat Ind.*, Dec. 1929, 21-3] recommend the Bömer test for differentiating lard and lard compounds, particularly those containing hydrogenated vegetable oils. Grossman describes a method of determining the molecular weight of higher saturated fatty acids and points out its application to the determination of lignoceric acid in mixtures containing hardened peanut butter. [*Z. Unters. Lebensm.*, 1929, 58, 209-61; *Brit. Chem. Abst.*, 1930, 381B; *Chem. Abst.*, 1930, 3390.] Grossfeld [*Apoth. Ztg.*, 1929, 44, 1387-91, 1403-6; *Chem. Abst.*, 1930,

742] states that the estimation of iso-oelic acid via Twitchell is of special importance for the recognition of hardened fats. Grossfeld also describes a method for separation of solid and liquid fats and for the detection of hardened fats in cacao butter. [*Chem. Umschau*, 1930, **37**, 3-13, 23-8; *Brit. Chem. Abst.*, 1930, 466B.] The determination of the thiocyanogen-iodine value combined with the iodine number offers the possibility of obtaining an insight into the linoleic acid and linoleic glyceride content of fats which are free from linolenic acid. [Waterman and Bertram, *J. Soc. Chem. Ind.*, 1929, **48**, 79-80T.]

6332. Acids and Esters. The monoalkyl esters and also the acid salts of various dibasic acids, such as oxalic, malonic and succinic acids, may be hydrogenated, according to Dreyfus [*Brit. Pat.* 316,158; *Brit. Chem. Abst.*, 1929, 807B] by treatment with hydrogen in the presence of reduced nickel at temperatures ranging from 15°-100° C. and at pressures of 100-150 atmospheres. Paal and Schiedewitz have noted the differing behavior of α - and β -chlorobutyric acids during catalytic hydrogenation. [*Ber.*, 1929, **62B**, 1935-9; *Brit. Chem. Abst.*, 1929, 1270A.] Catalytic reduction of the acid chloride of α -acetoxydiphenylacetic acid gives α -hydroxydiphenylacetaldehyde. [Zerner and Goldhammer, *Monatsh.*, 1929, **53** and **54**, 485; *Chem. Abst.*, 1930, 352.] Monocarboxylic acids are obtained from phthalic anhydride and other polycarboxylic acids and their derivatives such as diphenic, adipic, succinic, maleic or tartaric acids, by passing over catalysts which tend to split off carboxyl groups in the presence of hydrogen. [Jaeger, to Selden Co., *Brit. Pat.* 314,035, June 23, 1928; *Chem. Abst.*, 1930, 1123.] Acetic anhydride is hydrogenated (palladium-black), giving acetaldehyde and a little ethyl acetate. Reaction goes more readily in presence of hydrochloric acid. Propionic anhydride behaves similarly. Lauric anhydride is reduced with greater difficulty. [Mannich and Nadelmann, *Ber.*, 1930, **63B**, 796-9; *Brit. Chem. Abst.*, 1930, 740A.]

6333. Acetylene and Acetylenic Compounds. Fischer, Peters and Koch describe the catalytic hydrogenation and condensation of acetylene over an iron-copper-alkali catalyst. [*Brennstoff-Chem.*, 1929, **10**, 383-5; *Brit. Chem. Abst.*, 1929, 967B.] Ethyl acetylene may be obtained from methanol by electrolytic disaggregation of calcium carbide electrodes. This may be hydrogenated to *n*-butylene. [Dutt, French Pat. 677,338, Oct. 17, 1928; *Chem. Abst.*, 1930, 2956.] Acetaldehyde or acetic acid is prepared by passing acetylene over contact substances such as salts of mercury, silver, tin or copper preferably containing vanadium in the acid radical, in the presence of hydrogen and an oxidizing gas or substance liberating oxygen. [I. G. Farbenind. A.-G., French Pat. 645,967; *Chem. Abst.*, 1929, 1910.] In producing ethylene, acetylene and hydrogen are passed over aluminum powder, cerium, or cerium oxide, which may be mixed with active carbon, asbestos or kieselguhr. [I. G. Farbenind. A.-G., *Brit. Pat.* 325,695, Feb. 22, 1929; *Chem. Age* (London), 1930, 400; *Brit. Chem. Abst.*, 1930, 452B.] Polymerization of acetylene in the production of ethylene is minimized by adding 5-20 per cent by volume of water vapor to the acetylene-hydrogen mixture. [*Brit. Pat.* 325,152, Mar. 23, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abst.*, 1930, 408B.] The selective action of a palladium catalyst in the reduction of acetylenic compounds is described by Bourguel and Gredy. [*Compt. rend.* 1929, **189**, 757-9; *Brit. Chem. Abst.*, 1930, 79A.] They also suggest a mechanism for the reaction. [*Ibid.*, 1083-5; *Brit. Chem. Abst.*, 1930, 171A.] Isocrotonic acid is prepared by partial hydrogenation of tetrolic acid. Also, isostilbene is obtained from tolane. [Paal and Schiedewitz, *Ber.*, 1930, **63B**, 766-78; *Brit. Chem. Abst.*, 1930, 740A.] Hydrogenation of phenylpropionic acid in ethyl acetate yields primarily Liebermann's *alloisocinnamic* acid, together with its more stable transformation products, Erlenmeyer's *isocinnamic* acid, and *allocinnamic* acid, but no *trans*-isomeride. Acetylenedicarboxylic acid similarly yields maleic acid, and tolane gives isostilbene. Phenylpropionic alcohol yields *cis*-cinnamyl alcohol. [Bourguel, *Bull. Soc. chim.*, 1929, (iv), **45**, 1067-91; *Brit. Chem. Abst.*, 1930, 317A.] 1,1,1,3-Tetraphenylpropinene, $(C_6H_5)_3C \equiv CC(C_6H_5)_2$, is reduced in presence of platinic oxide (but not of palladium-black) to 1,1,1,3-tetraphenylpropane.

Also, 1-phenyl-3,3,3-tri-*p*-tolylpropinene gives 1-cyclohexyl-3,3,3-tri-*p*-tolylpropane. 1,1,4,4-Tetraphenylbutinene gives the saturated compound. 1,1,3-Triphenylpropinene, in presence of palladium-black, gives 1,1,3-triphenylpropane, and in presence of platonic oxide, 1-cyclohexyl-3,3-diphenylpropane. [Wieland and Kloss, *Ann.*, 1929, **470**, 201-23; *Brit. Chem. Abst.*, **1929**, 1053A.] Hydrogenation of 2,6-dimethyl-10-ethynylundecan-10-ol gives 2,6-dimethyl-10-vinylundecan-10-ol. [Fischer and Löwenburg, *Ann.*, 1929, **475**, 183-204; *Chem. Abst.*, **1930**, 595.] Catalytic hydrogenation of tetraphenylbutenediol in presence of colloidal palladium gives the highest yields of the β -tetraphenylbutenediol, when the reaction occurs slowly. Hydrogenation of either butenediol affords tetraphenylbutanediol. [Salkind and Teterin, *Ber.*, 1929, **62B**, 1746-50; *Brit. Chem. Abst.*, **1929**, 1067-8A. See also, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1751-7; *Brit. Chem. Abst.*, **1930**, 574A.] Hexinene-1,2,5,6-tetrol, in presence of colloidal platinum, absorbs one molecule of hydrogen, yielding Δ^2 -hexene-1,2,5,6-tetrol. 1,6-Dimethoxy- Δ^2 -hexane-2,5-diol is obtained similarly. [Lespieau and Bourguet, *Compt. Rend.*, 1930, **190**, 378-80; *Brit. Chem. Abst.*, **1930**, 450A.] 3,7-Oxido-3,7-dimethyl-octinene-1, in the presence of aqueous alcohol, hydrogen and a nickel catalyst, gives 3,7-oxido-3,7-dimethyloctane. [Rupe and Lang, *Helv. Chim. Acta.*, 1929, **12**, 1133-41; *Brit. Chem. Abst.*, **1930**, 61A.] 2,6-Di- β -phenylethynylpyridine, reduced by hydrogen and palladized barium sulphate to 2,6-distyrylpyridine. [Scheuing and Winterhalder, *Ann.*, 1929, **473**, 126-36; *Brit. Chem. Abst.*, **1929**, 1086A.]

6334. Poly-Hydroxylated Compounds. Glycerol, or its reduction product, propylene glycol, is obtained by catalytic hydrogenation of polyhydroxylated compounds in presence of metals of the iron or platinum group. Sorbitol at 200°-250° and 70-100 atmospheres pressure gives first, glycerol and then, propylene glycol; dextrose or sucrose is reduced at 150° and 40 atmospheres to the hexitol and then at 200°-250° and 150 atmospheres to glycerol and the glycol. Starch and cellulose are similarly reduced. [Brit. Pat. 299,373, Oct. 24, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abst.*, **1930**, 500B. See also French Pat. 662,874, Oct. 24, 1928; *Chem. Abst.*, **1930**, 378.] Formaldehyde or a polymer is boiled with a catalyst such as lead oxide in the presence of a mono- or poly-hydric alcohol miscible with water. The catalyst is separated and the solvent evaporated to obtain the sugar as a clear syrup. Thirty per cent aqueous formaldehyde, methyl alcohol and lead oxide may be thus treated; also trioxymethylene, glycerol and lead oxide; and formaldehyde, methyl alcohol and lime. The sugars may be reduced catalytically to obtain polyhydric alcohols. [I. G. Farbenind. A.-G., Brit. Pat. 327,193, Appln. date Dec. 3, 1928; *Chem. Age* (London), **1930**, 520.] Heptaacetylamygdalin in glacial acetic acid is converted by hydrogen and spongy palladium into heptaacetylgentiobiose. Hydrogenation of hexaacetylgentiobial affords hexaacetylhydrogentiobial. [Bergmann and Freudenberg, *Ber.*, 1929, **62B**, 2783-8; *Brit. Chem. Abst.*, **1930**, 70A.] Cellulosic material is treated with sulphuric acid and then mixed with calcium carbonate and heated with acetylene and hydrogen under pressure at 600° C. The gases formed are passed over nickel, pumice and copper, and an oil resembling crude petroleum is obtained. [Fischella, French Pat. 677,649, June 26, 1929; *Chem. Abst.*, **1930**, 3353.]

6335. Aldehydes. The vapor of crotonaldehyde mixed with hydrogen and preferably with steam is passed over a mixed copper and silver catalyst at 120° C., yielding butyl alcohol [Horsley and Imperial Chem. Industries, Ltd., Brit. Pat. 316,399, June 29, 1928; *Brit. Chem. Abst.*, **1929**, 806B.] Hydrogen is introduced through a perforated central pipe-lead and mixes gradually with crotonaldehyde vapor which contains steam. Over-heating is thus avoided. [Horsley and Imperial Chem. Industries, Ltd., Brit. Pat. 321,253, Aug. 22, 1928; *Brit. Chem. Abst.*, **1930**, 275B.] Hydrogenation of crotonaldehyde is secured without the use of steam and without formation of products of high boiling point by treating crotonaldehyde with hydrogen in the presence of a nickel catalyst at a temperature below 140° C. until most of the aldehyde has been converted into saturated compounds containing the propyl group; then treating the product with hydrogen at a higher temperature to produce butyl alcohol. [Holden,

assr. to Carbide & Carbon Chemicals Corporation, U. S. Pat. 1,724,761, Aug. 13, 1929; *Chem. Abst.*, 1929, 4712; *Brit. Chem. Abst.*, 1929, 1887B.] Butyl alcohol prepared by the catalytic hydrogenation of crotonic or butyric aldehyde is purified by treatment with chlorine or bromine or their hypo-acids. [I. G. Farbenind. A.-G., Brit. Pat. 312,512, June 20, 1928; *Chem. Abst.*, 1930, 865.] Aldehydes or ketones are catalytically hydrogenated to alcohols at pressures of 10–100 atmospheres which enables a gas mixture containing less than 80 per cent of hydrogen to be used. [Brit. Pat. 327,573, I. G. Farbenind. A.-G., April 6, 1929; *Chem. Age* (London), 1930, 562.] Aldol is reduced to 1,3-butylene glycol by passing it in the liquid or dissolved state together with hydrogen over a hydrogenating catalyst at temperatures of 50°–110°. Catalysts containing nickel, cobalt or copper may be used with or without activators such as alumina. [I. G. Farbenind. A.-G., Brit. Pat. 311,671, Feb. 9, 1928; *Chem. Abst.*, 1930, 865.] As a step in the process of making isoprene for conversion into artificial rubber, aldol is subjected to hydrogenation under the above conditions. [Brit. Pat. 320,362, March 30, 1928, I. G. Farbenind. A.-G.; *Chem. Age* (London), 1929, 551.] In producing mono- and poly-hydric alcohols by catalytic reduction with hydrogen of the condensation products of aldehydes or ketones, the condensing agent is removed from the condensation product previous to the reduction. [I. G. Farbenind. A.-G., Brit. Pat. 311,788, Dec. 2, 1927; *Chem. Abst.*, 1930, 861.] 2,3-Dimethoxybenzaldehyde, hydrogen and platinum-black, give 2,3-dimethoxybenzyl alcohol. [Montequi, *Anales soc. españ. fis. quim.*, 1929, 27, 692–4; *Chem. Abst.*, 1930, 605.] Ethylisoamylamine is converted by formaldehyde and hydrogen in presence of colloidal platinum into methylethylisoamylamine. When similarly treated with acetaldehyde, propaldehyde, and isobutaldehyde, the secondary amine affords diethylisoamylamine, ethyl-*n*-propylisoamylamine and ethylisoamylisoamylamine, respectively. Acetylacetone and dimethylamine affords δ -dimethylaminopentan- β -ol. Hydrogenation of a mixture of acetylbenzoyl and ethylamine leads to β -ethylamino- α -phenylpropan- α -ol, converted by reduction in presence of formaldehyde into β -methylethylamino- α -phenylpropan- α -ol. Catalytic reduction of benzoylacetone in presence of dimethylamine yields the two diastereoisomeric γ -dimethylamino- α -phenylbutan- α -ols. Catalytic reduction of acetylacetone in presence of ethylamine yields δ -ethylaminopentan- β -ol. [Skita and Keil, *Ber.*, 1930, 63B, 34–50; *Brit. Chem. Abst.*, 1930, 327A.] The hydrogenation of aliphatic acetals produces the mixed ether of ethyl and the acetal-forming alkyl, and the acetal-forming alcohol itself, in accordance with the reaction: $\text{CH}_3\text{CH}(\text{OR})_2 + \text{H}_2 = \text{C}_2\text{H}_5\text{OR} + \text{ROH}$. [Cabanac, *Compt. rend.*, 1929, 188, 1257–9; *Chem. Abst.*, 1929, 3900.] Aldehyde and ketone sulfoxylates are produced by reducing aldehyde or ketone bisulphites or aldehyde hyposulphites by hydrogen or by gases containing hydrogen, in the presence of a hydrogenation catalyst, and, generally, with or without increase of pressure, but when formaldehyde bisulphite is to be reduced an activated catalyst must be used or a pressure of at least 20 atmospheres must be employed. [I. G. Farbenind. A.-G., Brit. Pat. 308,229, Sept. 19, 1927; *Chem. Abst.*, 1930, 127.] Primary alcohols are obtained by treating an alkylene oxide with hydrogen in the presence of a hydrogenation catalyst, more particularly finely divided metals of the 8th group. A mixture of α - and β -butylene oxides yields butyl alcohols. Treatment of styrene oxide gives β -phenylethyl alcohol. [I. G. Farbenind. A.-G., Brit. Pat. 320,424, July 17, 1928; *Chem. Age* (London), 1929, 575; *Chem. Abst.*, 1930, 2468.]

6336. Ketones. Acetone is hydrogenated in the vapor phase in the presence of a catalyst containing copper and (or) silver and an oxide or hydroxide of a divalent metal. [Horsley and Imperial Chemical Industries, Ltd., Brit. Pat. 327,224, Jan. 25, 1929; *Chem. Age* (London), 1930, 520; *Brit. Chem. Abst.*, 1930, 602B.] Trifluoroacetone (CF_3COCH_3) is quantitatively and rapidly reduced to trifluoroisopropyl alcohol by hydrogen under 48 atmospheres in the presence of platinum-black. [Swarts, *Bull. soc. chim. Belg.*, 1929, 38, 99–109; *Chem. Abst.*, 1929, 4440–1.] To prepare 2-methyl-2,4-pentanediol, diacetone alcohol is treated with hydrogen and finely divided nickel at high temperature and pressure. [I. G. Farbenind. A.-G., Leopold-inventor, Ger. Pat. 486,767, Apr. 1, 1925; *Chem. Abst.*, 1930, 1870.] Pentan-2-ol-5-one and hydrogen in

the presence of platinum-black give pentan-2,4-diol. The latter is also obtained by the hydrogenation of acetylacetone. [Baudreughien, *Bull. sci. acad. roy. Belg.*, 1929, **15**, 53-80; *Chem. Abst.*, 1929, 4196.] Ethyl cyclopentyl ketone, when hydrogenated in acetic acid in presence of platinum-black, gives ethyl-cyclopentylcarbinol. [Vavon and Mitchovitch, *Bull. Soc. chim.*, 1929, iv, **45**, 961-72; *Brit. Chem. Abst.*, 1930, 206A.] Reduction of cyclohexylcyclohexanone by Skita's method gives *cis*-2-cyclohexylcyclohexanol. [Hückel, Neunhoeffer, Gercke and Frank, *Ann.*, 1929, **477**, 99-160; *Brit. Chem. Abst.*, 1930, 206A.] 5-Methoxy-4-ethoxyacetophenone, reduced to 5-methoxy-4-ethoxy-1-ethylbenzene. [H. Kondo and T. Kondo, *J. pr. Chem.*, 1930, ii, **126**, 24-52; *Brit. Chem. Abst.*, 1930, 794A.] Reduction of 2-cyclopentylcyclopentanone with sodium and alcohol gives the *trans*-alcohol in large amount, while catalytic reduction (Skita) affords mainly *cis*-2-cyclopentyl-cyclopentanol. [Hückel, Neunhoeffer, Gercke and Frank, *Ann.*, 1929, **477**, 99-160; *Brit. Chem. Abst.*, 1930, 206A.] *cis*-1-Propylcyclopentan-2-ol is obtained by hydrogenation of the corresponding ketone in presence of platinum-black in acetic acid containing hydrochloric acid. A mixture richer in the *trans*-isomeride is obtained in absence of hydrochloric acid. [Vavon and Flurer, *Bull. Soc. chim.*, 1929 (iv), **45**, 754-762; *Brit. Chem. Abst.*, 1929, 1290A.] Methyl ethyl ketone is condensed with formaldehyde to form methyl-2-keto-3-butanol and this is catalytically hydrogenated to 2-methyl-1:3-butylene-glycol. [Brit. Pat. 320,362, March 30, 1928. I. G. Farbenind. A.-G.; *Chem. Age* (London), 1929, 551.] Hydrogenation of 2-ethylcyclohexanone in presence of platinum-black in acetic and hydrochloric acid yields *cis*-2-ethylcyclohexanol. [Vavon and Mitchovitch, *Bull. Soc. chim.*, 1929, iv, **45**, 961-72; *Brit. Chem. Abst.*, 1930, 206A.] $\gamma\gamma$ -Diphenyl- α -hydrindone resists reduction by sodium and alcohol or catalytic hydrogenation. [Gagnon, *Ann. chim.*, 1929, x, **12**, 296-343; *Brit. Chem. Abst.*, 1930, 90A.] In connection with the oxidation of lobelanine, Wieland and Dragendorff obtained a neutral fraction which when hydrogenated in the presence of palladium-black yielded 1,7-dibenzoyl-*n*-heptane. Catalytic reduction of the neutral fraction in the presence of acetic acid gave 1,9-diphenyl-*n*-nonane-1,9-diol. [*Ann.*, 1929, **473**, 83-101; *Brit. Chem. Abst.*, 1929, 1085A.] Buck and Jenkins describe the following reductions which have been effected with almost quantitative yields: benzil, anisil, and piperil to the corresponding benzoin and hydrobenzoin derivatives; furil to furoin; phenyl benzyl ketone to phenylbenzylcarbinol; anisyl-methoxybenzyl ketone to $\alpha\beta$ -di-*p*-anisylethyl alcohol, and piperonyl *mp*-methylene-dioxybenzyl ketone to $\alpha\beta$ -dipiperonylethyl alcohol. [*J. Amer. Chem. Soc.*, 1929, **51**, 2163; *Brit. Chem. Abst.*, 1929, 1072A.] The hydrogenation of aldehydes and ketones to alcohols and of aldehyde alcohols to glycols is carried out in presence of oxide catalysts such as oxides of beryllium, magnesium, zinc, aluminum, silicon, titanium, germanium, zirconium, tin, cerium, thorium, vanadium, bismuth, chromium, molybdenum, tungsten, uranium, manganese, iron or rare earths, and substances are added to prevent dehydrating effects of the catalyst such as compounds of the alkali or alkaline earth metals of groups 1 and 2 in the form of oxides, carbonates, hydroxides or salts with weak acids such as organic acids. [Lazier (to E. I. DuPont de Nemours & Co.), Brit. Pat. 312,043, and -4, May 18, 1928; *Chem. Abst.*, 1930, 860.] Amino alcohols are prepared by the catalytic hydrogenation of a hydroxy-carbonyl compound, a polyhydroxy-carbonyl compound or a polycarbonyl compound, in the presence of ammonia or an amine. [Skita and Keil, Brit. Pat. 313,617, June 16, 1928; *Chem. Abst.*, 1930, 1119.] Phenyl α -oximinoethyl ketone is hydrogenated almost quantitatively in presence of hydrogen chloride (3 mols) and palladized charcoal to α -hydroxy- α -phenyl-isopropylamine hydrochloride. *p*-Tolyl α -oximinoethyl ketone is similarly reduced to the hydrochloride of α -hydroxy- α -*p*-tolyl-isopropylamine. [Hartung and Munch, *J. Am. Chem. Soc.*, 1929, **51**, 2262-6; *Brit. Chem. Abst.*, 1929, 1066A.]

6337. Amino-Ketones. Phenylmethylaminopropanol (ephedrine) is prepared by reducing phenyl methylaminoethyl ketone by hydrogen in the presence of finely divided platinum. [Fourneau, French Pat. 659,882, Dec. 23, 1927; *Chem. Abst.*, 1929, 5196.] Fourneau and Barrelet [*Anales soc. españ. fis. quim.*, 1929, **27**, 500-7; *Chem. Abst.*,

1930, 352] have prepared three higher homologs of ephedrine. These are phenyl- α -methylaminopropylcarbinol, phenyl- α -methylaminoisobutylcarbinol and 2-benzyl-2-methylaminoisopropanol, prepared by reducing the corresponding ketone by means of hydrogen in presence of platinum. De Buruaga has prepared a homolog of ephedrine by catalytic reduction of *p*-tolyl α -methylaminoethyl ketone to *p*-tolyl- α -methylaminocarbinol. [*Anales soc. espan. fis quim.*, 1929, 27, 712-6.] *l*-1-Phenyl-2-methylaminopropanol-1 and *d*-1-phenyl-2-methylamino-propanol-1, production by catalytic hydrogenation. [Brit. Pat. 318,488, Sept. 3, 1928, to I. G.; *Chem. Age* (London), 1929, 479.] Ketones of the type represented by *N*-methyl-3:4-dihydroxyphenacylamine, when hydrogenated in alkaline solution in the presence of nickel catalyst, yield amino-alkylarylcarbinols or *N*-alkylaminoalkylarylcarbinols. [Soc. Chem. Ind. in Basle, Brit. Pat. 296,006, Aug. 22, 1928; *Brit. Chem. Abst.*, 1929, 807B.] A mixture of acetylbenzoyl and dimethylamine on reduction gives *dl*-*N*-methylephedrine as does a mixture of acetylbenzoyl, methylamine and formaldehyde. [Skita and Keil, *Monatsh.*, 1929, 53 and 54, 753-63; *Brit. Chem. Abst.*, 1929, 1436A; *Chem. Abst.*, 1930, 336.]

6338. Nitro-Compounds. Williams has obtained high yields of aniline by the reduction of nitrobenzene vapor with hydrogen at 310° with tin oxide catalysts. No evidence was obtained of the reduction of the oxide to the metal in the experiments, and it was, moreover, found that normal specimens of tin do not catalyze this reaction at this temperature, which happens to be above the melting point of tin. [*Trans. Faraday Soc.*, 1929, 25, 446-51; *Brit. Chem. Abst.*, 1929, 1021A; *Chem. Abst.*, 1929, 4874.] Busch and Schulz have made a study of the catalytic reduction of nitro compounds using palladized calcium carbonate (1 per cent) as the catalyst and hydrazine as the source of hydrogen. [*Ber.*, 1929, 62B, 1458-66; *Chem. Abst.*, 1929, 4938.] *p*-Glycolylaminonitrobenzene may be treated with hydrogen under pressure in the presence of nickel to reduce to the amino-group. [Brit. Pat. 318,491, Sept. 3, 1928, to I. G.; *Chem. Age* (London), 1929, 479.] *o*- and *p*-Nitroethylbenzene in acetic acid and in presence of platinum-black are hydrogenated to *o*- and *p*-ethylaniline. [Vavon and Mitchovitch, *Bull. Soc. chim.*, 1929, iv, 45, 961-72; *Brit. Chem. Abst.*, 1930, 206A.] Methyl ethyl *p*-nitrophenyl-ethyl-malonate is reduced by catalytic hydrogenation with platinum oxide to the amino-derivative. [Bousquet and Adams, *J. Am. Chem. Soc.*, 1930, 52, 224-9; *Chem. Abst.*, 1930, 1086.] Ethyl-*bis*-(4-nitrophenyl)-methane is reduced in alcohol in presence of Adams' platinum catalyst and hydrogen to give ethyl-*bis*-(4-aminophenyl)-methane in quantitative yield. [Hussey, Marvel and Hager, *J. Amer. Chem. Soc.*, 1930, 52, 1124.] β -Nitro- α ,2,5-trimethoxy-3,4-methylenedioxyethylbenzene is reduced by either hydrogen and platinum-black under pressure or by sodium amalgam to the amino-derivative. [Mannich and Falber, *Arch. Pharm.*, 1929, 267, 601-9.] Reduction of dinitroabietic acid gives an undefined nitrogen-containing product. The amount of hydrogen absorbed is 1.74 mols. [Goldblatt, Lowy and Burnett, *J. Am. Chem. Soc.*, 1930, 52, 2132-6; *Chem. Abst.*, 1930, 3019.] Jaeger describes catalysts for production of hydrogenated organic nitrogen compounds. [Brit. Pat. 304,640, Jan. 23, 1928; *Chem. Abst.*, 1929, 4709.] 2:4-Dinitro-1-methylnaphthalene, reduced by platinum-black and hydrogen, gives 2-nitro-4-amino-1-methylnaphthalene. [Vesely, Stursa, Olejnick and Rein, *Coll. Czeck. Chem. Comm.*, 1929, 1, 493-515; *Brit. Chem. Abst.*, 1929, 1288A.]

6339. Nitriles. Tertiary amines are formed in the reduction of nitriles alone or in mixture with carbonyl compounds in basic solution. Skita and Keil describe the hydrogenation of acetonitrile, propionitrile, butyronitrile, valeronitrile, *p*-methoxybenzonitrile, and *p*-hydroxybenzonitrile. They also describe the hydrogenation of these nitriles in presence of cyclohexanone. [*Monatsh.*, 1929, 53 and 54, 753-63; *Brit. Chem. Abst.*, 1929, 1436A; *Chem. Abst.*, 1930, 336.] Catalytic hydrogenation of nitriles under reduced pressure has been carried out by Escourrou [*Bull. Soc. chim.*, 1929, (iv), 45, 735-44; *Brit. Chem. Abst.*, 1929, 1298A.] When hydrogenated at 190° under a pressure of 240 mm., phenylacetonitrile affords mainly phenylacetalimine, together with a little ethylbenzene and β -phenylethylamine; at 200° under a pressure

of 220 mm. the aldimine is obtained alone. Benzonitrile is converted in presence of nickel at 175° under a pressure of 10–11 mm. into benzaldimine. β -Hydroxy- α -phenylacetaldehyde is produced by the catalytic reduction of β -hydroxy- α -phenylacrylonitrile and subsequent hydrolysis of the aldimine obtained thereby. [Rupe, Swiss Pat. 120,517, Feb. 5, 1926; *Brit. Chem. Abst.*, 1930, 51B.] Anisaldehyde is readily converted by hydrogen in presence of nickel into anisyl alcohol, transformed by the usual methods into *p*-anisylacetonitrile, which is reduced to β -*p*-anisylethylamine. [von Braun, Bahn and Münch, *Ber.*, 1929, 62B, 2766–76; *Brit. Chem. Abst.*, 1930, 73A.] Catalytic hydrogenation (pyrophoric nickel) of β -methylpentane- $\alpha\gamma$ -dicarboxylonitrile results in the direct production of about 30 per cent of the disubstituted piperidine, hexahydro- β -collidine, owing to simultaneous hydrogenation and cyclization. [De Montmollin and Martenet, *Helv. Chim. Acta*, 1929, 12, 604–9; *Brit. Chem. Abst.*, 1929, 1078A.] The reduction, with nickel as a catalyst, of cyano-ketones and cyano-acids gives always the product most suitable for ring formation, if this is at all possible. The reduction of ethyl phenylecyanopyrrolacetate goes as far as the primary amine which splits off ethyl alcohol with closing of the 5-ring to give 4-phenyl-2,3-diketopyrrolidine. Ethyl benzoylcyanacetate gives ethyl α -benzoylpropionate. Ethyl benzylideneacyanoacetate gives the half-aldehyde of benzylmalonic acid and a new amino acid, α -benzyl- β -aminopropionic acid. [Rupe and Pieper, *Helv. Chim. Acta*, 1929, 12, 637–49; *Chem. Abst.*, 1929, 4463.] A mixture of hydrogen and hydrocyanic acid gas passed over a hydrogenating catalyst such as a platinum catalyst at a temperature of 150°–170° forms methylamine. [Barsky, to American Cyanamid Co., U. S. Pat. 1,736,872, Nov. 26, 1929; *Chem. Abst.*, 1930, 630; *Brit. Chem. Abst.*, 1930, 602B.]

6340. Reduction of Other —N=C— Linkages. 2-Ethylcyclohexanone oxime, hydrogenated in aqueous alcohol in presence of hydrochloric acid and platinum-black, yields 2-ethylcyclohexyl- β -hydroxylamine. [Vavon and Mitchovitch, *Bull. Soc. chim.*, 1929, iv, 45, 961–72; *Brit. Chem. Abst.*, 1930, 206A.] Hydrogenation of methyl-*p*-methoxyphenylglyoxime gives an equilibrium mixture of two isomers, methyl-*p*-methoxyphenylfuroxane and methyl-*p*-methoxyphenylglyoxime peroxide. [Ponzio, *Gazz. chim. ital.*, 1929, 59, 713–7; *Chem. Abst.*, 1930, 845.] Catalytic reduction of fluorene oxime in acetic acid gives hexahydroaminofluorene. [Nakamura, *Proc. Imp. Acad. (Japan)*, 1929, 5, 469–72; *Chem. Abst.*, 1930, 1637.] Catalytic hydrogenation of isonitrosoacetone converts it into *trans*-2,5-dimethylpiperazine. [Godchot and Mousseron, *Compt. rend.*, 1930, 190, 798–800; *Brit. Chem. Abst.*, 1930, 617A.] The semicarbazone of 1-propylcyclopentan-2-one, when hydrogenated in aqueous hydrochloric acid, yields the hydrochloride of 1-propylcyclopentyl-2-semicarbazide. [Vavon and Flurer, *Bull. Soc. chim.*, 1929, (iv), 45, 754; *Brit. Chem. Abst.*, 1929, 1290 A.] The semicarbazone of 1, 3-dipropylcyclopentan-2-one gives 1, 3-dipropylcyclopentany-2-semicarbazide. [*Idem, ibid.*, 1929 (iv), 45, 763; *Brit. Chem. Abst.*, 1929, 1299A.] Hydrogenation of laevul-*p*-toluidide anil, followed by hydrolysis of the product, affords 1-phenyl-2-methyl-5-pyrrolidone. The *p*-tolylimide of laevulanilide gives *p*-toluidine and 1-*p*-tolyl-2-methyl-5-pyrrolidone. [Lukes and Prelog, *Coll. Czech. Chem. Comm.*, 1929, i, 617–23; *Brit. Chem. Abst.*, 1930, 322A.] Compounds of the type $R(NH \cdot N = C_6H_4 = NOH)_2$, obtained by the action of benzoquinone monoxime on the dihydrazides of various dibasic acids, are reduced by hydrogen and colloidal palladium in normal sodium hydroxide solution to give *p*-aminobenzenehydrazo derivatives, $R(NHNHC_6H_4 \cdot NH_2)_2$. [Borsche, Müller and Bodenstein, *Ann.*, 1929, 475, 120–31; *Brit. Chem. Abst.*, 1929, 1438A.]

6341. Azoimide. The reducing action of molecular hydrogen on an alkaline solution of axoimide in presence of colloidal palladium is very slight, but in acid solution reduction takes place to completion with the formation of ammonia and hydrazine. The latter product is recognized after separation of the colloidal palladium by dialysis. The same result is obtained by the action of nascent hydrogen from zinc or iron and hydrochloric acid. The equation $HN_2 + 6H = NH_3 + N_2H_4$ is suggested. [Ricca and Pirrone, *Gazzetta*, 1929, 59, 379–84; *Brit. Chem. Abst.*, 1929, 1150A.]

6342. Nitrosoamines. Reduction of diphenylnitrosoamine in alcoholic solution in presence of palladized calcium carbonate or barium sulphate gives, almost quantitatively, nitrogen and diphenylamine. Nitrosopiperidine gives nitrogen, piperidine and piperylhydrazine. Di-*n*-propylnitrosoamine affords nitrogen, di-*n*-propylamine and di-*n*-propylhydrazine. *p*-Nitrosodimethylaniline is hydrogenated to *p*-aminodimethylaniline. [Paal and Yao, *Ber.*, 1930, **63B**, 57-66; *Brit. Chem. Abst.*, 1930, 336A.]

6343. Nitrogen-Heterocyclic Compounds. Piperidine and its homologs are made by hydrogenating pyridine and its homologs with hydrogen and a nickel catalyst under a pressure of 180-300 lb. per square inch. [Technical Research Works, Ltd., and Lush, *Brit. Pat.* 309,300, March 31, 1928; *Chem. Abst.*, 1930, 382.] 2-Phenacetylpyridine is hydrogenated, with a nickel catalyst, to form 2-phenylhydroxyethylpyridine; on further hydrogenation with platinum as catalyst, 2-phenylhydroxyethylpiperidine is formed. [Boehringer, *Brit. Pat.* 312,919, June 1, 1928; *Chem. Abst.*, 1930, 862.] Wibaut and Van de Lande have studied the formation of aminopyridine by the action of ammonia on pyridine in presence of catalysts. [*Rec. trav. chim.*, 1929, **48**, 1005-9; *Brit. Chem. Abst.*, 1929, 1313A.] Catalytic reduction of 2,3-diphenylquinoline gives 2,3-diphenyl-1,2,3,4-tetrahydroquinoline-A. [Plant and Rosser, *J. Chem. Soc.*, 1929, 1861-70; *Chem. Abst.*, 1930, 117.] Hydrogenation of isoquinoline in acetic acid solution at the ordinary temperature, using platinum oxide as catalyst, gives tetrahydroisoquinoline. At 100° there results decahydroisoquinoline. [Ranado and Vidal, *Anal. fis. quim.*, 1930, **28**, 76-78; *Brit. Chem. Abst.*, 1930, 480A.] 1-(4-Methoxybenzyl)-6,7-dimethoxy-3,4-dihydroisoquinoline, reduced (palladium) to 6,7-dimethoxy-1-(4-methoxybenzyl)-1,2,3,4-tetrahydroisoquinoline. [H. Kondo and T. Kondo, *J. pr. Chem.*, 1930, ii, **126**, 24-52; *Brit. Chem. Abst.*, 1930, 794A.] Zelinski and Jurjev have investigated the catalytic hydrogenation of 1-methylpyrrole and the dehydrogenation of 1-methylpyrrolidine. [*Ber.*, 1929, **62B**, 2589-90; *Brit. Chem. Abst.*, 1929, 1461A.] According to Craig [*J. Am. Chem. Soc.*, 1930, **52**, 804-808; *Brit. Chem. Abst.*, 1930, 480A] pyrrole is best hydrogenated in presence of alcoholic hydrochloric acid and a platinum oxide-platinum-black catalyst. 1-Phenylpyrrole is reduced to 1-cyclo-hexylpyrrolidine. Pyrrole and substituted pyrroles are reduced in good yields to the corresponding pyrrolidines with a platinum oxide catalyst. [DeJong and Wibaut, *Rec. trav. chim.*, 1930, **49**, 237-46; *Brit. Chem. Abst.*, 1930, 479A; *Chem. Abst.*, 1930, 3011.] Indoxyl, naphthindoxyl, their homologs and acyl derivatives, are catalytically hydrogenated to obtain dihydroindoxyls. [I. G. Farbenind. A.-G., *Brit. Pat.* 326,523, Nov. 6, 1928; *Chem. Age* (London), 1930, 467. See also French Pat. 672,258, Mar. 29, 1929; *Chem. Abst.*, 1930, 2142.] Reduction of tetramethylpyrazine hydrochloride using a platinum oxide-platinum catalyst gives mixture of β - and γ -tetramethylpiperazines. [Kipping, *J. Chem. Soc.*, 1929, 2889-97; *Brit. Chem. Abst.*, 1930, 223A.] Hydrogenation of 2,5-dimethylpyrazine in presence of nickel or platinum-black gives *trans*-2,5-dimethylpiperazine. [Godchot and Mousseron, *Compt. rend.*, 1930, **190**, 798-800; *Brit. Chem. Abst.*, 1930, 617A.] Hydrogenated over nickel at 170°, octahydrophenazine gives etradecahydrophenazine. In presence of platinum-black, an isomeric tetradecahydrophenazine is obtained. [Godchot and Mousseron, *Compt. rend.*, 1930, **190**, 442-3; *Brit. Chem. Abst.*, 1930, 618A; *Chem. Abst.*, 1930, 3017.]

6344. Alkaloids and Their Derivatives. ψ -Anhydrodihydrolupinine, $C_{10}H_{15}N$, is obtained by reduction of ψ -anhydrolupinine with hydrogen and palladium. Anhydromethyl-lupinine, $C_{11}H_{15}N$, is reduced (palladium) to a mixture of anhydrodihydromethyl-lupinines, $C_{11}H_{21}N$. Anhydrolupinine, under reduction conditions similar to the above, yields a mixture of lupinanes, $C_{10}H_{21}N$, i.e., absorbs four atoms of hydrogen. [Clemo and Raper, *J. Chem. Soc.*, 1929, 1927-40; *Brit. Chem. Abst.*, 1929, 1318A.] Reduction of disinomenine by hydrogen in presence of colloidal palladium gives tetrahydrodisinomenine ($C_{15}H_{24}O_4N$). Similarly, ψ -disinomenine yields ψ -tetrahydrodisinomenine. [Goto, *Bull. Chem. Soc. Japan*, 1929, **4**, 129-32; *Brit. Chem. Abst.*, 1929, 1089A.] Reduction of 4-benzyloxy-2-3':4'-dimethoxy-styrylquinoline in presence of palladized charcoal, gives galipoline. 4-Methoxy-2-4'-hydroxy-3'-methoxy- and 4-methoxy-2-3'-

hydroxy-4'-methoxy-styrylquinoline are reduced catalytically to 4-methoxy-2- β -4'-hydroxy-3'-methoxy- and 4-methoxy-2- β -3'-hydroxy-4'-methoxy-phenylethylquinoline, respectively. [Späth and Papaioanou, *Monatsh.*, 1929, **52**, 129-140; *Brit. Chem. Abst.*, 1929, 1087A.] von Braun and Lemke have described various hydrogenated quinoline derivatives obtained by the hydrogenation of cinchonine under pressure in presence of reduced nickel. [*Ann.*, 1930, **478**, 176-96; *Brit. Chem. Abst.*, 1930, 485A; *Chem. Abst.*, 1930, 3242.] Catalytic reduction of nicotine hydrochloride with hydrogen and a platinum oxide-platinum-black catalyst gives a mixture of amines which contain about one part of hexahydronicotine to three parts of octahydronicotine. [Windus and Marvel, *J. Am. Chem. Soc.*, 1930, **52**, 2543.] Reduction of 2 : 6-di(benzoylmethylene)piperidine with hydrogen in presence of platinum oxide and pyridine at 40°-50° yields the isomeric unsaturated glycols, α (racemic)- and β (meso)-norlobelanidiene. [Wieland and Drishaus, *Ann.*, 1929, **473**, 102-118; *Brit. Chem. Abst.*, 1929, 1036A.] The amine-oxide of methyl 5-deoxydihydro-morphinate is converted by catalytic hydrogenation into the corresponding amine. [Speyer and Roell, *Ber.*, 1930, **63B**, 539-51; *Brit. Chem. Abst.*, 1930, 623A.] Hydrogenation of norlobelanine and its derivatives. [Scheuing and Winterhalder, *Ann.*, 1929, **473**, 126-36; *Brit. Chem. Abst.*, 1929, 1086A.] 6-Keto-13-vinylhexamorphenol methyl ether is reduced (palladized charcoal) to the octahydro-ether. [Cahn, *J. Chem. Soc.*, 1930, 702-5; *Brit. Chem. Abst.*, 1930, 795A.] Speyer and Roell describe the action of ozone on hydrogenated bases of the morphine series. [*Ber.*, 1930, **63B**, 539-51; *Chem. Abst.*, 1930, 3243.]

6345. Other Heterocyclic Compounds. The di-ethyl ester of chelidonic acid has been hydrogenated with platinum oxide to give diethyl hydropyrandicarboxylate and a small amount of the γ -hydroxy derivative. Hydrogenation in decalin gives a hydrate of the γ -hydroxyhydropyrandicarboxylic acid ester. [Davila, *Anales soc. españ. fis. quim.*, 1929, **27**, 637-46; *Chem. Abst.*, 1930, 368.] 6-(3,4-Methylenedioxy-styryl)-5-carbethoxypyronone is hydrogenated in presence of palladium to 6-(3,4-methylenedioxy-phenylethyl)-5-carbethoxypyronone. [Lampe and Sandrowski, *Rocz. Chem.*, 1930, **10**, 199-210; *Brit. Chem. Abst.*, 1930, 611A.] Pierce and Parks [*J. Am. Chem. Soc.*, 1929, **51**, 3384-7; *Chem. Abst.*, 1930, 109] have studied the effect of temperature on the reduction rate of furfural with the catalyst from PtO₂-H₂O. β -2-Furylacraldehyde is reduced with hydrogen at 80° and under a pressure of 20 atmospheres in alcoholic solution with a nickel catalyst to 2-furfurylacetaldehyde. Similar reduction of α -2-furyl- $\Delta\alpha\gamma$ -hexadien- ϵ -one at 100° gives γ -furfurylbutyl methyl ketone. Reduction of furfurylidenemesityl oxide at 140°-150° and under a pressure of 24 atmospheres yields β -2-tetrahydrofurylethyl isobutyl ketone. [Wienhaus and Leonhardi, *Ber. Schimmel*, 1929, 223-32; *Brit. Chem. Abst.*, 1929, 1309A.]

6346. Terpenes and Terpene-like Substances. Geraniol is reduced exclusively to tetrahydrogeraniol by means of platinum-black in alcohol; in ether, some 2,6-dimethyloctane is also formed. [Longinov and Margoliss, *Bull. Soc. chim.* (4), 1929, **45**, 156-67; *Chem. Abst.*, 1929, 4441.] Hexahydro- ψ -ionone has been synthesized according to Ishizaka's method [*Ber.*, 1914, **47**, 2453], the only modification being that the hydrogenation of the geraniol was carried out at 130° under pressure, a nickel catalyst supported on charcoal being used in place of platinum-black. [Heilbron and Thompson, *J. Chem. Soc.*, 1929, 889.] Reduction of geraniol with platinum-black gives the reactions C₁₀H₁₆O \rightarrow C₁₀H₂₀O \rightarrow C₁₀H₂₂O, the former reaction being more rapid than the latter. A small amount of ferrous sulphate represses the reaction velocity. Citronellal adds 1 mol hydrogen to give dihydrocitronellal. Addition of ferrous sulphate hinders reduction of the double bond, yielding citronellol, probably containing some dihydrocitronellol. A fatigued catalyst may be activated by shaking with air. [Suzuki, *Chem. News*, 1929, **139**, 153; *Chem. Abst.*, 1929, 5467.] Dipentene is hydrogenated (nickel) at high pressure and temperature to form menthane. [Brit. Pat. 327,924, July 7, 1929, to Schering-Kahlbaum A.-G.; *Brit. Chem. Abst.*, 1930, 604B.] The general opinion that on hydrogenation of aliphatic terpenes the double bond 6 is reduced first, secondly the functional group, and last the double bond 2, does not hold in all cases.

Citronellal is reduced to dihydrocitronellal, in which case the double bond 2 is reduced before the aldehyde group. [Sabety and Bleger, *Bull. Soc. chim.*, 1929, **45**, 497-8; *Chem. Abst.*, 1930, 55.] $\Delta^1:6$ -Menthenol on reduction by the Sabatier method gives a saturated alcohol. Hydrogenation does not take place when other reduction methods are used. [Sandborn, *Organic Syntheses*, 1929, **9**, 52-53; *Brit. Chem. Abst.*, 1929, 1986A.] Thymol is prepared by treating hydroxythymol with hydrogen with or without a solvent in the presence of a hydrogenating catalyst at a high temperature and under pressure until 2 atoms of hydrogen are fixed. In addition to a hydrogenating catalyst, a surface catalyst such as "franconite" may be used. Menthol is obtained by continuing the hydrogenation until 8 atoms of hydrogen are fixed. [Schering-Kahlbaum A.-G., French Pat. 664,520, Nov. 23, 1928; *Chem. Abst.*, 1930, 865. See also Brit. Pat. 301,087, Nov. 23, 1928; *Brit. Chem. Abst.*, 1930, 302B.] Crude synthetic menthol is purified by converting the isomeric alcohols into a mixture of acid esters of a polybasic acid such as phthalic acid. The ester mixture is then washed or crystallized from a saturated liquid hydrocarbon such as cyclohexane, methyl-cyclohexane or decahydronaphthalene. [Howards & Sons, Ltd., and Huggett, Brit. Pat. 325,509, Nov. 19, 1928; *Chem. Age* (London), 1930, 398; *Brit. Chem. Abst.*, 1930, 486B.] Catalytic hydrogenation of β -pinene at the ordinary temperature and in the presence of platinum yields pinane identical with that derived from α -pinene. [Lipp and Witgert, *Ber.*, 1930, **63B**, 411-6; *Brit. Chem. Abst.*, 1930, 610A; *Chem. Abst.*, 1930, 3002.] Catalytic reduction of pulegone with reduced nickel and hydrogen at 8 to 20 atmospheres' pressure and a temperature of 150° gives a colorless liquid of boiling point 90°-100° at 16 mm. [González, *Anales soc. españ. fis. quim.*, 1930, **28**, 247-61; *Chem. Abst.*, 1930, 2739.] α -Anisylidenepulegone is hydrogenated in presence of palladized charcoal to *p*-methoxybenzylmenthone. Piperonylidenepulegone is reduced similarly to 3,4-methylenedioxybenzylmenthone; furfurylidenepulegone to tetrahydro- α -furfurylmenthone; and cinamylidenepulegone to γ -phenylpropylmenthone. [Thoms and Soltner, *Arch. Pharm.*, 1930, **268**, 157-66; *Brit. Chem. Abst.*, 1930, 610A; *Chem. Abst.*, 1930, 3235.] Read, Waters, Robertson and Hughesdon [*J. Chem. Soc.*, 1929, 2068] have pointed out certain interesting features connected with the hydrogenation of piperitone. ω -Acetylcamphene is reduced by hydrogen in presence of spongy platinum to acetylisocamphane. [Lipp and Quaadvlieg, *Ber.*, 1929, **62B**, 2311-22; *Brit. Chem. Abst.*, 1929, 1308A.] Blackie describes the hydrogenation of dacrene and isodacrene with a platinum catalyst. [*J. Soc. Chem. Ind.*, 1930, 26T.] Catalytic reduction of elemol and its derivatives. [Ruzicka and van Veen, *Ann.*, 1929, **476**, 70-112; *Brit. Chem. Abst.*, 1929, 1458A.] Wienhaus and Scholz have studied some new crystalline compounds from essential oils and have prepared various hydrogenated derivatives from them. [*Ber. Schimmel*, 1929, 267-82; *Brit. Chem. Abst.*, 1929, 1308A.] Waterman, Dewald and Tulleners have carried out the hydrogenation of rubber. [*Erdöl u. Teer*, 1929, **22**, 403-4; *Chem. Abst.*, 1929, 5349.] The importance of hydrogenation in the perfume industry is noted by Gerhardt. [*Riechstoffind.*, 1929, **4**, 156-8; *Chem. Abst.*, 1930, 3321.]

6347. Hydrogenation of Sterols. α - and β -Dihydroergosterol absorb 1 mol of hydrogen in presence of palladium and give α -ergosterol. α - and β -Ergostadienone absorb 2 mols and give α -ergosterol. [Heilbron, Johnstone and Spring, *J. Chem. Soc.*, 1929, 2248-55; *Brit. Chem. Abst.*, 1929, 1443A.] Hydrogenation of either α - or β -isoergosterol gives α -ergosterol, 4 atoms of hydrogen being absorbed. [Heilbron and Spring, *J. Chem. Soc.*, 1929, 2807-10; *Chem. Abst.*, 1930, 1388.] The acetate of *u*-ergostadienol, ($C_{27}H_{44}O$), is hydrogenated (platinum) to give the acetate of *u*-ergostanol, ($C_{27}H_{48}O$). Likewise, *u*-ergostatrienol is converted into *u*-ergostanol. [Windaus and Auhagen, *Ann.*, 1929, **472**, 185-94; *Brit. Chem. Abst.*, 1929, 1065A.] Windaus, Bergmann and Lüttringhaus describe the hydrogenation of various derivatives of ergosterol peroxide. [*Ann.*, 1929, **472**, 195-201; *Brit. Chem. Abst.*, 1929, 1065A.] Dihydrodehydroergosterol (ergosterol-*F*) is reduced by platinum and hydrogen in acetic acid to *allo*- α -ergosterol acetate. [Windaus, Bergmann and Butte, *Ann.*, 1930, **477**, 268-78; *Brit. Chem. Abst.*, 1930, 338A.] Reduction of *ergotetraene-B* with hydrogen in presence of

platinum-black and acetic acid at 70° and 150 atmospheres gives a saturated hydrocarbon, $C_{27}H_{48}$. Similar reduction of *ergotetraene-A* gives an ill-defined, unsaturated substance. [Rygh, *Z. physiol. Chem.*, 1929, **185**, 99-104; *Brit. Chem. Abst.*, 1930, 203A.] Reduction of neoergosteryl acetate with hydrogen in presence of platinum and acetic acid affords a hydrocarbon, $C_{27}H_{48}$. [Bonstedt, *Z. physiol. Chem.*, 1929, **185**, 165-168; *Brit. Chem. Abst.*, 1930, 84A.] Zymosterol is reduced (palladium) to dihydrozymosterol. [Heilbron and Sexton, *J. Chem. Soc.*, 1929, 2255-7; *Brit. Chem. Abst.*, 1929, 1443A. See also Reindel and Weickmann, *Ann.*, 1929, **475**, 86-100; *Chem. Abst.*, 1930, 624.] Isocholesterol is not readily reduced by hydrogen and palladium at room temperature. [Drummond and Baker, *J. Soc. Chem. Ind.*, 1929, **48**, 232-8T; *Chem. Abst.*, 1929, 5339-40.] Cholesterilene, when reduced with hydrogen and palladium, gives a mixture of cholestane and ψ -cholestane. [Boe and Doran, *J. Chem. Soc.*, 1929, 2244-8; *Brit. Chem. Abst.*, 1929, 1432A.] Schönheimer, von Behring and Hummel have investigated the hydrogenation of cholesterol in the organism. [*Naturwiss.*, 1930, **18**, 156; *Brit. Chem. Abst.*, 1930, 493A.] Heilbron and Spring point out the relation between the color reactions and absorption spectra of sterols and their structure. [*J. Soc. Chem. Ind.*, 1929, **48**, 1113. Cf. *Biochem. J.*, 1930, **24**, 133-5; *Brit. Chem. Abst.*, 1930, 597A.]

6348. Miscellaneous Complex Compounds. The dihydro-compound of *p'*-methylchalcone has been prepared by means of hydrogen and colloidal palladium in alcoholic solution. [Stobbe and Bremer, *J. pr. Chem.*, 1929, ii, **123**, 1-60; *Brit. Chem. Abst.*, 1929, 1179A.] Trimethylphloretin is obtained by catalytic reduction of 6-hydroxy-4',2',4-trimethoxychalcone. [Wessely and Sturm, *Monatsh.*, 1929, **53** and **54**, 554-61; *Chem. Abst.*, 1930, 371.] Perhydrobixin is obtained by hydrogenation of bixin in presence of platinum oxide-platinum-black. [Kuhn and Ehmman, *Helv. Chim. Acta*, 1929, **12**, 904-915; *Brit. Chem. Abst.*, 1929, 1456A.] LaForge and Smith [*J. Amer. Chem. Soc.*, 1929, **51**, 2574-81] have found that in the reduction of rotenone with hydrogen (1 mol) in presence of palladized barium sulphate and acetone or platinum oxide and ethyl acetate, both dihydrorotenone and an acid, $C_{21}H_{24}O_6$, are formed. Both of these compounds may be converted by further hydrogenation into the same acid, $C_{21}H_{26}O_6$. [See also LaForge and Smith, *ibid.*, 1930, **52**, 1088-98.] Catalytic reduction of isorotenone gives the compound, $C_{21}H_{24}O_4$. Catalytic reduction of rotenic acid, obtained by the action of alcoholic-potash on isorotenone, gives dihydrorotenic acid. [Butenandt and Hildebrandt, *Ann.*, 1930, **477**, 245-68; *Chem. Abst.*, 1930, 1641; *Brit. Chem. Abst.*, 1930, 478A.] Pellitorine, when hydrogenated in methyl alcohol in presence of palladized charcoal, absorbs four atoms of hydrogen and gives tetrahydropellitorine, which has been shown to be *n*-deco-*iso*-butylamide. [Gulland and Hopton, *J. Chem. Soc.*, 1930, **6**.] Catalytic hydrogenation of porphyrins and chlorophyll compounds in glacial acetic acid by means of Adams' platinum oxide catalyst leads to leuco-compounds. The number of moles of hydrogen absorbed is three to four. [Conant and Hyde, *J. Amer. Chem. Soc.*, 1930, **52**, 1233-9.] Methyl vouacapenate, a crystalline ester obtained from the wood of *Vouacapoua americana*, gives a tetrahydro-derivative when reduced with hydrogen and platinum oxide or platinum-black. [Spelstra, *Rec. trav. chim.*, 1930, **49**, 226-36; *Chem. Abst.*, 1930, 3001.] Catalytic reduction of santonin yields a mixture of di- and tetrahydrosantonin. [Wedekind, Goost and Jackh, *Ber.*, 1930, **63B**, 50-6; *Brit. Chem. Abst.*, 1930, 347A.] Phytol is reduced with hydrogen and platinum oxide in absolute alcohol to dihydrophytol. [Kuhn and Sugimoto, *Helv. Chim. Acta*, 1929, **12**, 915-9; *Chem. Abst.*, 1930, 338.] Fischer and Löwenberg describe the synthesis of phytol by hydrogenation reactions. [*Ann.*, 1929, **475**, 183-204; *Chem. Abst.*, 1930, 595.] Dehydronorcholene by catalytic hydrogenation yields dehydronorcholane, ($C_{27}H_{48}$). [Wieland and Wiedersheim, *Z. physiol. Chem.*, 1930, **186**, 229-36; *Brit. Chem. Abst.*, 1930, 473A.] Triacetylsphingosine, when ozonized in acetic acid and the product subjected to catalytic reduction with palladium and hydrogen, yields myristic acid and myristic aldehyde. [Klenk, *Z. physiol. Chem.*, 1929, **185**, 169-82; *Chem. Abst.*, 1930, 859-60.] Farnesol has been hydrogenated

(nickel supported on charcoal) to hexahydrofarnesol. [Heilbron and Thompson, *J. Chem. Soc.*, 1929, 889-90.] Hydrogenation of methyl anhydro- γ -isodigitoxigenate gives the monomethyl ester of γ -digitoxanol-diacid. Methyl isodigitoxigenate could not be hydrogenated. [Jacobs and Gustus, *J. Biol. Chem.*, 1930, 86, 199-216; *Brit. Chem. Abst.*, 1930, 749A.]

6349. Nuclear Hydrogenation. Salicylic acid, when reduced in alcoholic solution with platinum-black and hydrogen at room temperature, yields 1-hydroxy-cyclohexane-2-carboxylic acid. Acetylsalicylic acid gives hexahydrobenzoic acid and acetic acid; phenyl salicylate, dodecahydrosalol; *m*-hydroxybenzoic acid, *cis*-3-hydroxycyclohexane-1-carboxylic acid; and *p*-hydroxybenzoic acid, *cis*-4-hydroxycyclohexane-1-carboxylic acid. [Balaš and Šrol, *Coll. Czech. Chem. Comm.*, 1929, 1, 658-67; *Brit. Chem. Abst.*, 1930, 212A.] Aromatic esters are hydrogenated in presence of nickel at 30-40 atmospheres and at 120°-150° C. The preparation of the following is described: ethyl hexahydrobenzoate; ethyl cyclohexylacetate; methyl hexahydrosalicylate; ethyl hexahydrophthalate; methyl hexahydroterephthalate; ethyl 5:6:7:8-tetrahydro-1-naphthoate; ethyl 5:6:7:8-tetrahydro-3-hydroxy-2-naphthoate, and ethyl 5:6:7:8-tetrahydro-3-amino-2-naphthoate. [I. G. Farbenind. A.-G., *Brit. Pat.* 286,201, January 7, 1929; *Brit. Chem. Abst.*, 1930, 136B.] Catalytic reduction of the isomeric forms of ethyl 1,2-dimethylbicyclohexane-4,5-dimalonate gives the two isomeric ethyl 1,2-dimethylcyclohexane-4,5-dimalonates. [Cawley, Evans and Farmer, *J. Chem. Soc.*, 1930, 522-30; *Chem. Abst.*, 1930, 2716.] Cyclohexadiene and acetaldehyde combine at 100° to give 2:5-endoethylene- Δ^1 -tetrahydrobenzaldehyde, which is reduced by hydrogen in presence of colloidal palladium and alcohol to 2:5-endoethylenehexahydrobenzaldehyde. Cyclohexadiene and dibromomaleic anhydride give 1:2-dibromo-3:6-endoethylene- Δ^4 -tetrahydrophthalic anhydride, converted by hydrogen into 3:6-endoethylene- Δ^1 -tetrahydrophthalic anhydride. Reduction of *cis*-3:6-endoethylene- Δ^4 -tetrahydrophthalic acid affords *cis*-3:6-endoethylenehexahydrophthalic acid. Cyclopentadiene and dibromomaleic anhydride condense in ether, forming 1:2-dibromo-3:6-endomethylene- Δ^4 -tetrahydrophthalic anhydride. Catalytic reduction of the latter compound (platinum-black) affords 3:6-endomethylene- Δ^1 -tetrahydrophthalic anhydride. [Diels and Alder, *Ann.*, 1930, 478, 137-54; *Brit. Chem. Abst.*, 1930, 472A; see also Diels and Alder, *Brit. Pat.* 300,130, Nov. 5, 1928, to the I. G.; *Brit. Chem. Abst.*, 1930, 549B.] With a platinum-oxide catalyst phenylacetaldehyde di-*n*-propylacetal gives hexahydrophenylacetaldehyde di-*n*-propylacetal. Cinnamaldehyde diethylacetal gives β -phenylpropaldehyde diethylacetal. Benzaldehyde diethylacetal gives a mixture of hexahydrotoluol, hexahydrobenzyl ethyl ether and hexahydrobenzyl alcohol. [Sigmund, *Monatsh.*, 1929, 53 and 54, 607-19; *Brit. Chem. Abst.*, 1929, 1449A.] 6-Carboxy-3-methyl-*cis*- Δ^4 -tetrahydrophthalic acid (palladium) gives 6-carboxy-3-methyl-*cis*-hexahydrophthalic acid. [Farmer and Warren, *J. Chem. Soc.*, 1929, 906-7.] Norton recommends hexahydrophthalide as the pressure transmitting medium in a system for hydraulic power transmission. [U. S. Pat. 1,764,032, June 17, 1930, assigned to Selden Co.] Crude benzol in the presence of molybdenum sulphide and cobalt oxide at 300° and under 60 atmospheres' pressure may be treated with hydrogen for both desulphuration and hydrogenation. [I. G. Farbenind. A.-G., *Brit. Pat.* 315,349, Jan. 14, 1928; *Chem. Abst.*, 1930, 1734; *Brit. Chem. Abst.*, 1929, 804B.] *L*-Hexahydrophenylalanine is prepared by the catalytic reduction (platinum) of *L*-tyrosine in presence of dilute hydrochloric acid. [Karrer and Kehl, *Helv. Chim. Acta*, 1930, 13, 50-63; *Brit. Chem. Abst.*, 1930, 339A.] The action of cyclohexane and its derivatives on organic compounds in the presence of aluminum chloride. [Bodroux, *Ann. chim.*, 1929, (10), 11, 511-82; *Chem. Abst.*, 1929, 4936.] Free amino-bases are hydrogenated in the liquid phase at 270°-300° under about 100 atmospheres' pressure in presence of reduced nickel or cobalt. Toluidines and xylydines give cyclohexylamines, and β -naphthylamine yields 50 per cent of *ar*- and 30 per cent of *ac*-tetrahydro- β -naphthylamine. [I. G. Farbenind. A.-G., *Brit. Pat.* 290,175, May 7, 1928; *Brit. Chem. Abst.*, 1929, 888B.]

For the liquid phase hydrogenation of arylamines such as ethylaniline or *o*-toluidine, the nickel or cobalt catalyst is mixed with sodium carbonate or calcium oxide. [I. G. Farbenind. A.-G., Brit. Pat. 295,033, Aug. 1, 1928; *Brit. Chem. Abst.*, 1930, 275B.] Hexahydroaniline. [Lommel and Goose, Ger. Pat. 481,984, Nov. 27, 1926. See Can. Pat. 283,752.] 1-Benzyl-4-piperidone hydrochloride, when reduced in 95 per cent alcohol with Adams' platinum oxide-platinum-black catalyst and hydrogen at 2 to 3 atmospheres' pressure gives 1-benzyl-4-piperidine hydrochloride. Under the same conditions 1-phenyl-4-piperidone hydrochloride forms 1-cyclohexyl-4-piperidine hydrochloride; that is, there is a simultaneous nuclear hydrogenation of the phenyl-group. [Bolyard, *J. Amer. Chem. Soc.*, 1930, 52, 1030; *Brit. Chem. Abst.*, 1930, 786A.] The action of oxygen on 1,4-dimethylcyclohexane. [Chavanne and Bode, *J. Am. Chem. Soc.*, 1930, 52, 1609-22; *Brit. Chem. Abst.*, 1930, 768A.]

6350. Naphthalene Derivatives. *ar*-Tetrahydronaphthylamines are prepared by hydrogenation of acylated naphthylamines and saponifying the products to obtain the free base. [Leopold Cassella & Co., G.m.b.H. (Klingermann, Korten, Lommel and Goose, inventors), Ger. Pat. 479,401, Oct. 11, 1925; *Chem. Abst.*, 1929, 4710.] Naphthol esters are catalytically hydrogenated to obtain *ar*-tetrahydronaphthol esters. The catalyst is a base metal, e.g., nickel, and an organic solvent such as tetra- or decahydronaphthalene may be added. [I. G. Farbenind. A.-G., Brit. Pat. 326,762, Nov. 16, 1928; *Chem. Age* (London), 1930, 493. See also French Pat. 644,408, Nov. 21, 1928; *Chem. Abst.*, 1930, 862.] A method of separating the isomeric decahydronaphthols consists in obtaining fractions rich, respectively, in the *cis*- and *trans*-forms, converting them into the corresponding phthalic or oxalic acid esters, separating, and reconverting to the hydronaphthol. [J. D. Riedel-E. de Haen A.-G., Hückel, inventor, Ger. Pat. 485,715, Oct. 15, 1926; *Chem. Abst.*, 1930, 1121.] Reduction of *trans*- α -ketodecahydronaphthalene with hydrogen in presence of acetic acid, colloidal platinum, chloroplatinic and hydrochloric acids at 50°, gives a *trans*- α -decahydronaphthol. [Hückel, Neunhoeffer, Gercke and Frank, *Ann.*, 1929, 477, 99-160; *Brit. Chem. Abst.*, 1930, 206A.] Reduction of 5,8-diacetoxy-1,4-dihydronaphthalene (colloidal palladium) gives 5,8-diacetoxy-1,2,3,4-tetrahydronaphthalene. [Diels, Alder and Stein, *Ber.*, 1929, 62B, 2377-72; *Brit. Chem. Abst.*, 1930, 1303A.] When hydrogenated under pressure dihydroxydinaphthyl- and phenyldihydroxydinaphthyl-methanes are converted into the corresponding xanthenes by elimination of water, the xanthene subsequently undergoing further hydrogenation and yielding, by fission of the molecule in two directions, hydrogenated naphthalenes or naphthols. [Ipatiev and Dolgov, *Bull. Soc. chim.*, 1929, iv, 45, 950-61; *Brit. Chem. Abst.*, 1930, 210A.] Naphthostyryl is treated with hydrogen under pressure in the presence of decahydronaphthalene and a hydrogenation catalyst, such as nickel, to obtain tetrahydronaphthostyryl. [Schlichenmaier and Kross, to General Aniline Works, U. S. Pat. 1,742,322, Jan. 7, 1930; *Chem. Abst.*, 1930, 1121.] β -Methylnaphthaquinone, dissolved in glacial acetic acid and in presence of platinum oxide, gives 2-methyl-1,4-dihydroxynaphthalene. [Madinaveitia and deBurnaga, *Anales soc. españ. fis. quim.*, 1929, 27, 647-58; *Chem. Abst.*, 1930, 358.] In the course of a study of the behavior of aromatic halogenated ethylenes toward sodium, Blum [*Ber.*, 1929, 62B, 881-93; *Chem. Abst.*, 1929, 3920] treated $(C_6H_5)_2C=CHBr$ in ether with sodium powder and on hydrolysis of the resulting product obtained a hydrocarbon, $C_{22}H_{22}$, which proved to be 1,2,4-triphenyl-1,4-dihydronaphthalene. It takes up 2 atoms of hydrogen on catalytic hydrogenation and forms chiefly the tetrahydronaphthalene derivative.

6351. Industrial Hydrogenation of Naphthalene. Schrauth describes a process for hydrogenating naphthalene. The hydrocarbon, preliminarily freed from catalyzer poisons, is treated with hydrogen at a temperature of 150° to 200° in the presence of a mixture of hydrogenation catalytic metal compounds such as nickel and cobalt salts. [U. S. Pat. 1,733,908, Oct. 29, 1929, to Newport Mfg. Co.; *Chem. Abst.*, 1930, 382.] Naphthalene is vaporized and purified by the action of sodium. It is hydrogenated without intermediate condensation. [Schrauth and Schroetter, U. S. Pat. 1,733,909;

Chem. Abst., 1930, 382.] Naphthalene, without being previously sulphurized, is treated with sodium under a high pressure of hydrogen (e.g., 100 atmospheres) at over 300° to produce hydronaphthalenes. [I. G. Farbenind. A.-G., Ger. Pat. 488,759, Dec. 3, 1921; *Chem. Abst.*, 1930, 2142.] Mixtures of sodium and potassium, for example, NaK or NaK₂, are more active catalysts than the single metals for hydrogenation of naphthalene. [French Pat. 609,786, April 28, 1925, to Comp. de Prod. Chim. et Electrometallurg. Alais, Froges, & Camargue; *Brit. Chem. Abst.*, 1930, 410B.] Tetrahydronaphthalene in pure form is obtained by hydrogenating naphthalene in the vapor phase under conditions precluding any condensation. A nickel catalyst is used. [Technical Research Works, Ltd., and Lush, Brit. Pat. 304,403, Nov. 4, 1927; *Chem. Abst.*, 1929, 4713.] Aromatic hydrocarbons are hydrogenated at temperatures above 350° in the presence of catalysts immune from sulphur poisoning and under conditions more strenuous than those required only for the purification of the crude material from the sulphur it contains. [Brit. Pat. 322,445, Sept. 3, 1928, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1930, 2755. See also French Pat. 667,241, Jan. 11, 1929; *Chem. Abst.*, 1930, 1119.] Schroetter describes the purification of naphthalene prior to hydrogenation by heating it with an alkali metal, finely divided iron or nickel, or fuller's earth. [U. S. Pat. 1,763,410, June 10, 1930, to Newport Mfg. Co.] Naphthalene, in molten condition, is atomized by a blast of a gas such as air in order to effect fractional crystallization from the resulting mixture. [Derby and Davis, U. S. Pat. 1,727,052, Sept. 3, 1929; *Chem. Abst.*, 1929, 5193.]

6352. Reactions of Hydrogenated Naphthalenes. Tetrahydronaphthalene and ethylene react under pressure at 100° C. in the presence of aluminum chloride to yield oily bodies. [Michel, U. S. Pat. 1,741,742, Dec. 31, 1929, and Reissue 17,548, Dec. 31, 1929. See also U. S. Pat. 1,766,344, June 24, 1930, to the I. G.] Naphthalene or tetrahydronaphthalene may be condensed with propylene and higher olefines in presence of aluminum chloride. [Brit. Pat. 295,990, Aug. 1, 1928, to the I. G. Addn. to Pats. 265,601 and 273,665. *Brit. Chem. Abst.*, 1930, 276B.] Other partly hydrogenated isocyclic polynuclear hydrocarbons such as acenaphthene, phenanthrene or anthracene may be condensed with olefine in presence of catalysts of the Friedel-Crafts type. [Brit. Pat., 323,100, Dec. 3, 1928, to the I. G.; *Chem. Age* (London), 1930, 182; *Chem. Abst.*, 1930, 2758.] The condensation products may be used in varnishes. [French Pat. 676,508, June 11, 1929, to the I. G.; *Chem. Abst.*, 1930, 3122.] Zelinski and Turova-Pollak describe the behavior of *cis*- and *trans*-decalin toward bromine and aluminum bromide. [*Ber.*, 1929, 62B, 1658-63; *Chem. Abst.*, 1930, 105.] Tetralin and palladium-black reduce cinnamic acid, oleic acid, eugenol and coumarin to hydrocinnamic acid, stearic acid, hydroeugenol and hydrocoumarin, respectively, the first three at 115°-120° and the last in boiling toluol. [Akabori and Suzuki, *Proc. Imp. Acad.*, Japan, 1929, 5, 255-6; *Chem. Abst.*, 1929, 4671.] Decalin and tetralin have been subjected to a cracking process in a modified Rittman apparatus at different pressures and temperatures. [Butkov, *Neftyanoe Khozyaistvo*, 1928, 15, 674-8; *Chem. Abst.*, 1929, 4333.] Treatment of decalin with hydrogen under high pressure results in a mixture of naphthenes, probably substituted derivatives of cyclohexane. [Ipatiev, Orlov and Lukhachev, *J. Russ. Phys.-Chem. Soc.*, 1929, 61, 1339-43; *Chem. Abst.*, 1930, 1730.] Hydrolysis of naphthenic acids at elevated temperatures and cracking under pressure of hydrogen. [Ipatiev and Petrov, *Zhur. Prikladnoi Khim.*, 1929, 2, 327-35; *Chem. Abst.*, 1929, 4453. Cf. *Ber.*, 1930, 63B, 329-31; *Chem. Abst.*, 1930, 2732.] $\Delta^{9:10}$ -Octahydronaphthalene. [Nametkin and Glagolev, *J. Russ. Phys.-Chem. Soc.*, 61, 535-40, 1929; *Chem. Abst.*, 1929, 4465. See also Hückel, Danneel, Schwartz and Gercke, *Ann.*, 1929, 474, 121-44; *Brit. Chem. Abst.*, 1930, 76A.]

6353. Uses of Hydrogenated Naphthalenes. For the recovery of volatile solvents, Brégeat prefers tetralin for solvents immiscible with water. As an absorbent for benzol it has the advantage that it does not resinify or increase in viscosity. [Hock, *Inst. Chem. Eng.*, Dec. 6, 1929, 43-6; *Brit. Chem. Abst.*, 1930, 39B.] For the extraction of acetic acid from its aqueous solutions Suida [Brit. Pat. 303,494, Jan. 5, 1928; *Chem.*

Abst., 1929, 4711] uses a mixture of a base such as quinoline or dimethylaniline and a hydrocarbon material such as hydrogenated naphthalene and oils obtained from the destructive hydrogenation of coal. Jellies have been prepared by dispersing palmitates, stearates, oleates, ricinoleates, and linoleates in tetrahydronaphthalene and decahydronaphthalene. [Da Fano, *Ind. olii min. e grassi*, 1929, 9, 105-8; *Chem. Abst.*, 1929, 5386.] Tetralin has been suggested as a surface-tension-reducing agent in the destructive hydrogenation of coal. [Brit. Pat. 309,228, Oct. 3, 1927, to the I. G.; *Chem. Abst.*, 1930, 490.] In a study of the low-temperature carbonization of coal in the presence and absence of tetrahydronaphthalene, Kreulen has found that the yields of coke, tar, liquor, and gas, and the quality of the coke, were the same as obtained by carbonizing the coal directly. [*Brennstoff-Chem.*, 1929, 10, 382-3; *Brit. Chem. Abst.*, 1929, 966B.] A transparent potassium soft soap may be mixed with decahydronaphthalene and methanol at 60° to form a cleaning agent. [von Schwarzenstein, Swiss Pat. 133,808, Sept. 30, 1927; *Chem. Abst.*, 1930, 1759.] Soap emulsions of the acetyl, benzoyl, and crotonaldehyde derivatives of hydrogenated naphthalene are stated to be better insecticides, etc., than hydrogenated naphthalene itself. [J. D. Riedel A.-G., Ger. Pat. 453,193, Oct. 11, 1924; *Brit. Chem. Abst.*, 1930, 298B.] Tetrahydronaphthalene sulphonic acid is recommended for use as tanning and wetting agents. [Brit. Pat. 302,938, Dec. 22, 1928, to the I. G. See also Daimler and Balle, Ger. Pat. 459,045, July 23, 1924, to the I. G.; *Brit. Chem. Abst.*, 1930, 548B.] Tetrahydronaphthalene is added to ordinary gasoline in proportions of about one ounce per five gallons in order to lessen carbon formation from its use in internal combustion engines. [Fessler, U. S. Pat. 1,749,244, March 4, 1930; *Chem. Abst.*, 1930, 2285.] A mixture of potassium hydroxide, coal tar bases, and hydrogenated hydrocarbons has been suggested for extracting the impurities from crude anthracene. [Brit. Pat. 319,762, Sept. 29, 1928, to Rutgerswerke A.-G. and Kahl; *Chem. Abst.*, 1930, 2582.] "Hydrated" naphthalene is subjected to electrical discharges and the product is used in varnishes. [Becker, U. S. Pat. 1,754,186, April 8, 1930; *Chem. Abst.*, 1930, 2622.] Tetralin is used as a thinner in printing inks containing cellulose esters or ethers and rubber. [Morris, Brit. Pat. 320,410, July 13, 1928; *Chem. Abst.*, 1930, 2622.]

6354. Anthracene and Derivatives. Complete reduction of 1-hydroxyanthracene gives octahydroanthracene. Intermediate compounds are 1-hydroxy-9,10-dihydro-, 1-keto-1,2,3,4-tetrahydro-, and 1-hydroxy-1,2,3,4-tetrahydro-anthracene. 2-Hydroxyanthracene gives analogous compounds. 1-Aminoanthracene gives 1-amino-1,2,3,4,5,6,7,8-octa- and 1-amino-5,6,7,8-tetrahydroanthracene. [von Braun and Bayer, *Ann.*, 1929, 472, 90-121; *Brit. Chem. Abst.*, 1929, 1057A.] Anthraquinone derivatives are reduced by treating them in a non-acidic medium with hydrogen at high temperatures and pressures and in presence of the usual base metal hydrogenating catalysts. The reaction occurs in steps. When anthraquinone is reduced, anthrone or anthranol is formed as the first phase in practically quantitative yield. In the second phase, tetrahydroanthranol is formed and further hydrogenation gives octahydroanthranol. The final product is octahydroanthracene. [von Braun and Bayer, U. S. Pat. 1,751,670, March 25, 1930, to General Aniline Works, Inc. See also U. S. Pats. 1,758,381 and -2 May 13, 1930; *Chem. Abst.*, 1930, 3248.] Reduction of Δ^2 -tetrahydroanthraquinone in presence of colloidal palladium yields 1,2,3,4-tetrahydroanthraquinone. [Diels, Alder and Stein, *Ber.*, 1929, 62B, 2337-72; *Brit. Chem. Abst.*, 1929, 1303A.] Crude anthracene is purified by extracting the impurities by means of tetrahydrofurfuryl alcohol. [Norton, U. S. Pat. 1,764,031, assignor to Selden Co., June 17, 1930.] Crude anthracene is heated at high temperature under pressure by the Bergius process and the volatile products are mixed with benzene to obtain an "anti-knock" motor fuel. [French Pat. 630,326, March 5, 1927, to Soc. Internat. des Combustibles Liquides, assocs. of Deutsche Bergin-A.-G. f. Kohle u. Erdölchem.; *Brit. Chem. Abst.*, 1930, 48B.]

6355. Other Poly-Nuclear Compounds. The pressure hydrogenation product of fluorene (which, in addition to the true perhydride, always contains a mixture of its cleavage products) has been subjected by Orlov and Belopolski to berginization at 380°

under 70–5 atmospheres' initial hydrogen pressure. The light fraction of the product (up to 150°) contains a mixture of monocyclic naphthenes and another fraction gives indications of the presence of bicyclic naphthenes. [Ber., 1929, 62B, 1226–34; Chem. Abst., 1929, 4465. Cf., J. Russ. Phys. Chem. Soc., 1929, 61, 1267–77; Brit. Chem. Abst., 1930, 331A.] In conformity with the conclusions drawn from the earlier work of Orlov and his associate Lichachev, chrysene heated under hydrogen pressure has been found to give phenanthrene and its tetrahydride and also benzene, its homologs and hydrides, and naphthalene hydrocarbons. [Ber., 1929, 62B, 719–22; Chem. Abst., 1929, 3926; see also Ber., 1929, 62B, 710.] 1,1-Diphenylhydrindene, obtained by catalytic reduction of 1,1-diphenylindene. [Gagnon, Ann. chim., 1929, x, 12, 296–343; Brit. Chem. Abst., 1930, 90A.] Chloroindane, by the chlorination and hydrogenation of the indene from coal tar. [Ger. Pat. 492,510, March 28, 1926, to Comp. Nationale de Matières colorantes et manufactures de produits chimiques du Nord réunies, Etab. Kuhlmann; Chem. Abst., 1930, 2474.] Zelinski and Semiganovski describe the distillation of rosin acid in presence of aluminum chloride. An oil capable of being hydrogenated over platinum is obtained. [Ber., 1929, 62B, 2202–5.] Reduction of pimaric acid with hydrogen in presence of colloidal platinum and acetic acid at 60° yields a dihydropimaric acid, C₃₀H₄₈O₂. [Balaš and Brzák, Coll. Czech. Chem. Comm., 1929, 1, 352–59; Brit. Chem. Abst., 1929, 1076A.] Reduction (platinum and hydrogen) of d-pimarol gives dihydro-d-pimarol. [Balaš, Casopis Ceskoslov. Lek., 1927, 7, 320–38; Chem. Zentr., 1929, i, 2530–2531; Brit. Chem. Abst., 1929, 1499A.] Staudinger and his collaborators have studied the hydrogenation of various highly polymerized compounds. Polyindene. [Staudinger, Johner, Schiemann and Wiedersheim, Helv. Chim. Acta, 1929, 12, 962.] Polystyrene. [Staudinger and Wiedersheim, Ber., 1929, 62B, 2406–11; Brit. Chem. Abst., 1929, 1287A.] Caoutchouc, gutta-percha and balata. [Staudinger, Ber., 1930, 63B, 921–34; Brit. Chem. Abst., 1930, 782A.]

6356. Phenols and Phenolic Compounds. The reaction equilibrium resulting from the thermal decomposition and from the reduction with hydrogen and with carbon of phenol and *m*-cresol is treated thermodynamically by Hagemann. [Z. angew. Chem., 1929, 42, 503–8; Chem. Abst., 1929, 5402.] Aromatic hydrocarbons are prepared from vaporized phenols by the action of hydrogen at high temperatures. One of the reacting gases is heated to the required high temperature and then allowed to mix with the other. [Irinnyi, Ger. Pat. 481,732, June 13, 1924; Chem. Abst., 1929, 5193.] *o*-Ethylphenol, in acetic acid and in presence of platinum-black, affords a mixture of *cis*- and *trans*-2-ethylcyclohexanols. [Vavon and Mitchovitch, Bull. Soc. chim., 1929, iv, 45, 961–72; Brit. Chem. Abst., 1930, 206A.] Reduction of 2-hydroxydiphenyl by Adams' method gives *cis*-2-cyclohexylcyclohexanol. [Hückel, Neunhoeffer, Gercke and Frank, Ann., 1929, 477, 99–160; Brit. Chem. Abst., 1930, 206A.] von Braun and collaborators have studied the diphenylmethane derivatives obtained by condensation of ketones with aromatic amines and phenols. They describe a number of hydrogenation reactions. [von Braun, Anton, Haensel and Werner, Ann., 1929, 472, 1–89; Brit. Chem. Abst., 1929, 1058–61A.] Alkylisopropylphenols and alkylcoumaranes are obtained by the thermal decomposition of condensation products prepared from *m*- and *p*-cresol and aliphatic ketones, in the presence of a metal hydrogenation catalyst. [Chemisch Fabrik auf Actien vorm. E. Schering and Jordan, Brit. Pat. 306,051, Aug. 15, 1927; Chem. Abst., 1929, 4949; Jordan, U. S. Pat. 1,679,664, Aug. 7, 1928; Brit. Chem. Abst., 1930, 135B; Brit. Pat. 293,001, June 23, 1928, addn. to 276,010 and 280,956; Brit. Chem. Abst., 1930, 136B; Brit. Pat. 320,638, July 17, 1928, to Schering-Kahlbaum A.-G.; Chem. Age (London), 1929, 575.] Isopropenyl-*m*- and -*p*-cresols are di- or octahydrogenated at 140°–160° or 170°–180° in presence of nickel to give thymol, 3-isopropyl-*p*-cresol, menthol, or 4-methyl-6-isopropylcyclohexanol. [Chem. Fabr. auf Actien vorm. E. Schering, Brit. Pat. 273,685, June 15, 1927; Brit. Chem. Abst., 1930, 136B. See also Brit. Pat. 309,865, April 16, 1928; Chem. Abst., 1930, 626; French Pat. 672,995 April 11, 1929; Chem. Abst., 1930, 2142.] The condensation product of acetone and *m*-cresol may be acylated prior to hydrogenation. [Schoeller, Jordan and Clerc,

U. S. Pat. 1,737,272, Nov. 26, 1929; *Chem. Abst.*, 1930, 630. See also Brit. Pat. 293,874 July 13, 1928, addn. to 273,685; *Brit. Chem. Abst.*, 1930, 218B.] Primary and secondary amines may be made by passing amines or ammonia with alcohols or phenols and hydrogen at a high temperature and with or without pressure over a hydrogenation catalyst. Hydrogenated phenols may be used without hydrogen. [I. G. Farbenind. A.-G., French Pat. 669,824, Feb. 18, 1929; *Chem. Abst.*, 1930, 1866. See also Brit. Pat. 306,414, Feb. 18, 1928.] A mixture of acids obtained by oxidation of hydrogenated phenols is esterified by a mixture of aliphatic, aromatic or cyclic alcohols. *Cyclohexanol*, obtained by the hydrogenation of the phenol, and hydrogenated crude cresol may be used. [Deutsche Hydrierwerke A.-G., Ger. Pat. 484,904, Jan. 21, 1926, addn. to 434,730; *Chem. Abst.*, 1930, 1120. See also Ger. Pat. 483,822, Jan. 21, 1926; *Chem. Abst.*, 1930, 2141.] Reduction of resorcinol with hydrogen in presence of water, alcohol, or decalin and a nickel-cobalt-copper catalyst at 100° to 125° affords a mixture of *cis*- and *trans*-*cyclohexane*-1,3-diol. Similar hydrogenation of phloroglucinol in decalin gives 30 per cent of a mixture of α - and β -*cyclohexane*-1,3,5-triol. [Lindemann and Baumann, *Ann.*, 1929, 477, 78-98; *Brit. Chem. Abst.*, 1930, 209A.] Observations on the electrolytic reduction of phenol at various cathodes. [Bancroft and George, *Trans. Am. Electrochem.*, 57, preprint, 1930; *Chem. Abst.*, 1930, 2059; *Brit. Chem. Abst.*, 1930, 553A.]

6357. Uses of Hydrogenated Phenols. Materials such as starch, dextrin, vegetable gums, gelatin, glue or casein are dissolved in organic solvents insoluble in water by use of a solubilizing agent comprising a soap or soap-like substance in aqueous solution together with a water-soluble organic solvent such as a hydrogenated phenol. [Oranienburger Chemische Fabrik A.-G., Brit. Pat. 307,079, Mar. 2, 1928; *Chem. Abst.*, 1929, 5284.] Compositions suitable for removing water-soluble stains from artificial silk or other materials previous to treatment of the material with the usual dry cleaning liquid comprise soap, water, and a substance such as *cyclohexanol*, *cyclohexanone* and their homologs, which is readily soluble in the dry cleaning liquid to be used and is also somewhat soluble in or miscible with water. [Hubbard (to British Celanese, Ltd.), Brit. Pat. 307,508, Mar. 10, 1928; *Chem. Abst.*, 1929, 5332.] Emulsions for washing and bleaching comprise a soap, one or more hydrogenated aromatic compounds, and bentonite. [Industrial Processes Development, Ltd., Ger. Pat. 482,417, Feb. 16, 1923; *Chem. Abst.*, 1930, 520.] A motor spirit containing 15 to 20 per cent water with homogenizing agents such as hydrogenated phenols, cyclic ketones, cyclic alcohols (for example, *cyclohexanol*) and soap, together with the usual spirit such as benzine, benzol, or petroleum, is suggested by Schieweck. [Ger. Pat. 488,934, Aug. 15, 1925; *Chem. Abst.*, 1930, 2274.] The preignition of fuels which tend to detonate is prevented by the addition of at least 5 per cent of hydrogenated phenols. [Ger. Pat. 457,581, Jan. 20, 1925, to Deutsche Hydrierwerke A.-G.; *Brit. Chem. Abst.*, 1930, 314B.] Copper nitrate is dissolved in methyl*cyclohexanol* and the solution added to a motor fuel to prevent knocking. [Brit. Pat. 267,079, Aug. 12, 1926, to Continentale A.-G. f. Chemie; *Brit. Chem. Abst.*, 1928, 81B.] Condensation products of phenol and aliphatic aldehydes in the intermediate or "B" stage are dissolved in cyclic ketones or alcohols, hydrogenated naphthalenes or phenols, with or without addition of oils. The solutions are used as lacquers. [Bakelite Ges.m.b.H., Brit. Pat. 295,335, Aug. 9, 1928; *Brit. Chem. Abst.*, 1930, 469B.]

6358. Hydrogenation of other Carbonaceous Materials. Light hydrocarbons are obtained from carbonaceous materials by treatment with nascent hydrogen, under 5 atmospheres' pressure and at a temperature between 200° and 1000°. [Fohlen, French Pat. 670,508, June 20, 1928; *Chem. Abst.*, 1930, 1969. See also Fohlen, French Pat. 670,077, June 15, 1928; *Chem. Abst.*, 1930, 1970.] Oils or tars are converted into products of low boiling point by heating in the presence of organic amides or amines, such as formamide, acetamide, hexamethylenetetramine or aniline, with or without aldehydes or ketones containing more than four carbon atoms per molecule (suitably under pressure with hydrogen) at temperatures of 410°-600°. [I. G. Farbenind. A.-G.,

Brit. Pat., 320,421, July 7, 1928; *Chem. Abst.*, 1930, 2594.] The gases and vapors from destructive hydrogenation are recovered by strong cooling or great compression. By releasing the pressure on the washing oil which has been caused to absorb the gases and low boiling point substances, a gaseous mixture of hydrogen and hydrocarbons is obtained. [I. G. Farbenind. A.-G., Brit. Pat. 319,657, Sept. 25, 1928; *Chem. Abst.*, 1930, 2864.] Hydrogen which is first obtained may be purified and reused in the process of hydrogenation, and hydrocarbons such as propane, butane and pentane next obtained may be isolated. [I. G. Farbenind. A.-G., Brit. Pat. 322,734, Sept. 3, 1928; *Chem. Abst.*, 1930, 2865. See also French Pat. 675,789, May 27, 1929; *Chem. Abst.*, 1930, 2865.] The fraction boiling between 80° and 150° C. is used to extract bituminous materials or residues of destructive hydrogenation products. Other solvents such as alcohols or ketones may be added if desired. [Brit. Pat. 322,749, Sept. 6, 1928, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1930, 2876.] Oils are obtained by extracting the waste products of distillation residues of destructive hydrogenation with liquid sulphur dioxide. [I. G. Farbenind. A.-G., Ger. Pat. 486,309, Jan. 6, 1927; *Chem. Abst.*, 1930, 1961.] High boiling hydrocarbons, particularly lubricating oils, may be obtained by treating carbonaceous materials with a solvent under pressure, and treating the extracted products with hydrogen at a higher temperature but not sufficiently high to cause appreciable dissociation. [French Pat. 675,073, May 15, 1929, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1930, 2874. See also Brit. Pat. 323,791, Sept. 11, 1928; *Chem. Abst.*, 1930, 3345.] Lubricating oils are obtained by condensation of mineral oils or hydrogenation products in the presence of a gas containing oxygen or sulphur or in the presence of a halogen, and then treating the product with hydrogen at a high temperature and pressure and, if necessary, in the presence of a catalyst. [French Pat. 676,089, June 3, 1929, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1930, 2874.] The high-boiling crude oils, such as lubricating oils obtained by hydrogenation, are purified by treatment with acids or alkalies and distillation *in vacuo*. [Brit. Pat. 323,805, Oct. 11, 1928, to the I. G.; *Chem. Abst.*, 1930, 3353.] Crude paraffin is purified by treatment with hydrogen at 300° to 400° C. and pressure from 10 to 250 atmospheres. Under these conditions little or no dissociation of the paraffin itself occurs. Catalysts such as molybdic acid may be used. [Brit. Pat. 320,921, July 19, 1928, to the I. G.; *Chem. Abst.*, 1930, 2595. See also French Pat. 673,823, April 22, 1929; *Chem. Abst.*, 1930, 2595.] Bituminous fuels are treated with hydrogen at a raised temperature and pressure until sufficient fuel to act as binder for the remainder has been converted into a pitchy mass. The material is then compressed into briquettes for fuels. [Hilger, Ger. Pat. 494,085, Sept. 3, 1926; *Chem. Abst.*, 1930, 2864.] Ipatiev and Ivanov describe results obtained by heating the primary tar from a Donetz-Reviere coal under hydrogen pressure. [*Ber.*, 1930, 63B, 331-4; *Chem. Abst.*, 1930, 2862.] Pertierra has hydrogenated a Spanish long-flame gas coal. [*Anal. soc. españ. fis. quim.*, 1930, 28, 389-415; *Chem. Abst.*, 1930, 3343.] In tests upon the distillation of coal under pressure and in the presence of hydrogen, Leroux concludes that for a given distillation temperature there is a pressure for which the gas calories are a maximum. [*J. Usines a Gaz.*, 316, July 5; *Chim. et ind.*, 903, Dec. 1929.] Lategan describes experiments on the hydrogenation of coal from the Witbank Central Area, Transvaal. He concludes that the ease of hydrogenation of a coal is dependent on the readiness with which it dissociates into its molecular complexes, and on the composition and stability of these. [*Third Empire Min. Met. Congr.*, Apr., 1930, 21 pp.; *Brit. Chem. Abst.*, 1930, 541B.] Tanaka and Fujisawa have carried out the catalytic hydrogenation of shale oil under high pressure (140-150 atmospheres) and at temperatures of 280°-290°. The process results in increased yields of solid paraffin, decreased pitch and gas, and decreased refining loss by sulphuric acid. Reduced nickel was employed as catalyst. They consider that the more unsaturated high-boiling hydrocarbons are catalytically hydrogenated to hydrocarbons of less unsaturation, or to the saturated hydrocarbons without inducing any great cracking of the hydrocarbons. [*J. Soc. Chem. Ind., Japan*, 1930, 33, No. 2, 42-3B; *Chem. Abst.*, 1930, 2868; *Brit. Chem. Abst.*, 1930,

599B.] The sulphur content of impure oils may be reduced by hydrogenation at temperatures of 300°–400° and pressures above 20 atmospheres in presence of catalysts of the sixth group or of cobalt and its compounds. The unsaturated content of the oils is also reduced. [Brit. Pat. 300,900, Nov. 6, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abst.*, 1930, 499B.] Production of refined hydrocarbon oils by hydrogenation. [Brit. Pat. 327,463, Nov. 6, 1928, addn. to 300,900; *Brit. Chem. Abst.*, 1930, 599B.] Crude benzol is freed from sulphur by treating with hydrogen at increased temperature and pressure. The crude benzol may be mixed with a middle oil or with coal or may be used to extract coal or destructive hydrogenation residues, the mixture being then treated with hydrogen. The temperature may be 380°–550° C., and the pressure up to 1000 atmospheres. The catalyst may consist of molybdic acid, zinc oxide, magnesia and chromic acid. [I. G. Farbenind. A.-G., Brit. Pat. 327,194, Dec. 3, 1928; *Chem. Age* (London), 1930, 520; *Brit. Chem. Abst.*, 1930, 546B.] Water-gas is used to hydrogenate the desulphurized gases from lignite or tar to obtain a liquid fuel. [Joseph, U. S. Pat. 1,758,796, May 13, 1930, to Soc. intern. des proc. Prud'homme Houdry; *Chem. Abst.*, 1930, 3345.]

6359. Other Hydrogenation Processes. In the hydrogenation of carbonaceous materials such as topped American petroleum, the residual material not appreciably affected by the first stage of treatment is separated and treated under more "vigorous" conditions. A three-stage hydrogenation process may be carried out in the successive stages of which there are used, respectively, temperatures of 400°, 450° and 460°, and catalysts containing tungsten, molybdenum and chromium, and molybdenum and zinc. [Brit. Pat. 320,473, I. G. Farbenind. A.-G., Aug. 31, 1928; *Chem. Abst.*, 1930, 2875.] Crude oil is mixed with about an equal quantity of bituminous material of not less than 20 per cent volatile content and the mixture is heated to 180° at atmospheric pressure in a still having stirrers formed of or plated with nickel. After products of low boiling point have been volatilized and condensed, the temperature is raised to 320° and the pressure to 200 lb. per sq. in. and steam is admitted. The distillation is continued until the residue consists of a mixture of petroleum-pitch and coke suitable for use as a fuel. [Cranston, Brit. Pat. 322,167, Aug. 24, 1928; *Chem. Abst.*, 1930, 2875.] A two-stage process consists of heating coal under pressure without hydrogen, then proceeding to a second step in which the products are subjected to heat treatment in presence of hydrogen and with or without catalysts. [French Pat. 35,205, April 19, 1928, addn. to 647,742, to the I. G.; *Chem. Abst.*, 1930, 2138.] Coal is converted by hydrogenation at a high temperature and pressure into a mixture of heavy oils and pitch, and this mixture is subjected to further treatment in a separate vessel in which heavy oils from a preceding batch are simultaneously re-treated. [Deutsche Bergin.-A.-G. für Kohle- und Erdölchemie (Debo, inventor), Ger. Pat. 494,213, July 31, 1926; *Chem. Abst.*, 1930, 2865.] The material to be treated is passed with hydrogen through a preheating system thence into a converter where hydrogenation occurs. The temperature is controlled by circulation through a heater. [Tate and Stephenson, Imperial Chemical Industries, Ltd., Brit. Pat. 327,443; *Chem. Age* (London), 1930, 541.] In preheating carbonaceous materials from 300° to the temperature required for destructive hydrogenation, the heat is supplied to the materials in admixture with part of the hydrogenating gas. Brown coal may be mixed with a high boiling point coal hydrogenation product. [I. G. Farbenind. A.-G., Brit. Pat. 322,489, Sept. 3, 1928; *Chem. Abst.*, 1930, 2864. See also French Pat. 676,270, June 6, 1929; *Chem. Abst.*, 1930, 2865.] The reaction vessel may be heated by circulating hydrogen at a suitable temperature, e.g., 450°, through a surrounding jacket, and all or part of this hydrogen is then admitted into the reaction vessel together with the preheated coal, oil, etc. [Tate, Stephenson and Imperial Chem. Industries, Ltd., Brit. Pat. 326,238, Dec. 8, 1928; *Brit. Chem. Abst.*, 1930, 498B; *Chem. Age* (London), 1930, 443.] The relatively cold substance to be hydrogenated is caused to flow first on to the internal face of the walls of the hydrogenating vessel, or to flow between the walls of the vessel and the reaction chamber and is then introduced into the reaction chamber. [French Pat. 674,614, May 6, 1929,

Imperial Chemical Industries, Ltd.; *Chem. Abst.*, 1930, 2865.] Jaeger describes apparatus and procedure applicable to hydrogenation reactions. [Brit. Pat. 306,442, Feb. 20, 1928, to Selden Co.; *Chem. Abst.*, 1929, 4851. See also Brit. Pat. 306,519, Feb. 23, 1928; *Chem. Abst.*, 1929, 4851.] Two forms of apparatus for hydrogenating oil or liquid pastes are described by Tate and Stephenson. [Brit. Pat. 326,586, Dec. 31, 1928; *Chem. Age* (London), 1930, 468; *Brit. Chem. Abst.*, 1930, 498B. Brit. Pat. 326,896, same date, to Imperial Chemical Industries, Ltd.; *Chem. Age* (London), 1930, 494; *Brit. Chem. Abst.*, 1930, 546B.]

6360. Catalysts Used for Carbonaceous Materials. According to Reichenbach, molybdenum and its compounds at temperatures above 300° and at high pressures have given good results in the hydrogenation of coal. Certain sulphides like cadmium and iron sulphides; tungsten and chromium compounds; nitrogen derivatives; mixtures of copper with zinc, cadmium, boron, aluminum, silicon, titanium, vanadium or tantalum; and oxides of chromium, zinc and manganese have proved effective under certain conditions. Not only the composition, but also the physical condition of the catalyst is important. [*Metallbörse*, 1929, 19, 2861; *Chem. Abst.*, 1930, 1957.] In order to avoid accumulation in the lower parts of the reaction vessel, catalysts immune to sulphur poisoning are employed in colloidal dispersion. [Brit. Pat. 326,184, Sept. 3, 1928, to the I. G.; *Chem. Age* (London), 1930, 442; *Brit. Chem. Abst.*, 1930, 498B.] It is also suggested to prevent formation of sludges during hydrogenation by subjecting the paste to vigorous stirring by a rotary device. [Brit. Pat. 326,157, Sept. 3, 1928, to the I. G.; *Chem. Age* (London), 1930, 442; *Brit. Chem. Abst.*, 1930, 498B.] During hydrogenation the catalyst may be heated by radiation from suitable surfaces, which preferably consist of metals or oxides of the iron group which have a high heat absorption. [Brit. Pat. 327,025, April 15, 1929, to the I. G.; *Chem. Age* (London), 1930, 294; *Brit. Chem. Abst.*, 1930, 493B.] Catalysts are, prior to the reaction, irradiated by Röntgen rays, rays of radioactive substances, etc. [Brit. Pat. 315,900, to the I. G.; *Brit. Chem. Abst.*, 1929, 939B.] The catalyst or the member on which it is distributed is in the form of a surface of revolution of a catenary. The wall surrounding the catalyst is of similar shape, and has a number of discharge passages. [Soc. Anon. D'Ougree Marihay, Brit. Pat. 327,378, April 7, 1928; *Chem. Age* (London), 1930, 520; *Brit. Chem. Abst.*, 1930, 493B.] Naphthalene and low-temperature tar benzines are hydrogenated under pressure and at elevated temperatures, using as catalyst the residual coal which remains as the insoluble and undistillable portion of the original coal after hydrogenation according to the Bergius process. [Kaffer, Brit. Pat. 302,912, Dec. 18, 1928, to Ges. f. Teerverwertung m.b.H.; *Brit. Chem. Abst.*, 1930, 546B.]

6361. Hydrogenation of Carbon Monoxide. Natta has examined the promoting action of various oxides on zinc oxide in the methanol synthesis. Oxides which act as promoters are of two kinds: (1) Certain bivalent oxides such as magnesium, nickel, copper, cobalt, iron, and manganese, which have ionic diameters varying between 0.60 and 0.90 Å. These pass into solid solution in the zinc oxide lattice, and their activity is the greater the more they deform the lattice. (2) Oxides which remain in a finely divided amorphous or colloidal state and prevent the growth of the zinc oxide granules, for example, aluminum and chromium oxides. [*Giorn. Chim. Ind. Appl.*, 1930, 12, 13-23; *Brit. Chem. Abst.*, 1930, 552A.] In a study of promoter action on a cobalt-copper catalyst for the reduction of carbon monoxide at ordinary pressure, Kodama finds that magnesium oxide is most efficient; beryllium oxide is a poor promoter, and zinc oxide poorer still. Cadmium acts as a poison. [*J. Soc. Chim. Ind. Japan*, 1930, 33, 60B; *Brit. Chem. Abst.*, 1930, 551A.] Alcohols other than methanol are synthesized from carbon monoxide and hydrogen in the presence of a methanol catalyst to which an alkali metal has been added, and using a space velocity of the reacting gases which is more than five times that which the methanol synthesis employing only the methanol catalyst would reach equilibrium under the same temperature and pressure conditions. [Brit. Pat. 323,240, E. I. DuPont de Nemours & Co., June 22, 1928;

Chem. Abst., 1930, 3022.] Metal halides which are not decomposed by the reaction are added to the catalysts for the same purpose. [Brit. Pat. 323,513, I. G. Farbenind. A.-G., Sept. 1, 1928; *Chem. Abst.*, 1930, 3022.] Low-boiling and unsaturated hydrocarbons are obtained from carbon monoxide and hydrogen at high temperature and pressure using catalysts which contain metals of the eighth group of the periodic system together with alkali metal compounds and small quantities of sulphur, selenium, or tellurium in a free or combined state. The liquid olefinic hydrocarbons are useful as "anti-knock" motor fuels. [Brit. Pat. 322,284, Oct. 11, 1928, to I. G. Farbenind. A.-G.; *Chem. Abst.*, 1930, 2874; French Pat. 677,973, July 6, 1929; *Chem. Abst.*, 1930, 3247.] The water which is formed in the catalytic hydrogenation of carbon monoxide is removed in solid form by cooling the mixture to low temperatures. [I. G. Farbenind. A.-G., Ger. Pat. 492,427, Jan. 3, 1924, addn. to 479,829, Wietzel and Luther, inventors; *Chem. Abst.*, 1930, 2755.] Gases containing carbon monoxide for the methanol synthesis are purified by passing over iron oxide at a temperature of 400° to 850° to remove sulphur. [Bannister, U. S. Pat. 1,757,826, May 6, 1930, to Commercial Solvents Corp.; *Chem. Abst.*, 1930, 3292.] Jaeger proposes various catalysts for the reduction of oxides of carbon or organic compounds containing oxygen. [Brit. Pat. 306,471, Feb. 21, 1928, to Selden Co.; *Chem. Abst.*, 1929, 4949.] Tongue describes the high-pressure chemical engineering equipment of the Chemical Research Laboratory at Teddington. The apparatus includes low-pressure gas-storage, compression plant, a high-pressure gas-storage, distribution system, high-pressure autoclaves, and other apparatus for catalytic reactions. [*Inst. Chem. Eng.*, Apr. 1930. Advance proof.] Insecticides are produced by hydrogenating the residues from the manufacture of isobutyl alcohol. [Dobmaier and Kukenthal, Ger. Pat. 496,102, July 3, 1928, to the I. G.; *Chem. Abst.*, 1930, 3333.] The high-boiling alcohols obtained by the hydrogenation of carbon monoxide are mixed with a low-boiling alcohol, soap and a low-boiling hydrocarbon to form a cleansing and emulsifying agent. [Punga, U. S. Pat. 1,757,441, May 6, 1930, to the I. G.; *Chem. Abst.*, 1930, 3332.]

6362. Hydrogen. Larsson recommends the reaction between copper phosphide and superheated steam as a method of producing phosphoric acid and hydrogen. [U. S. Pat. 1,756,429, April 29, 1930, to DuPont Ammonia Corp.; *Chem. Abst.*, 1930, 3090.] Hydrogen and carbon dioxide may be obtained by introducing air and steam into the regions of blast furnaces situated above the fusion zone. [Heyd, French Pat. 676,196, June 5, 1929; *Chem. Abst.*, 1930, 2714.] Lock states that hydrogen and the corresponding hydroxy-acid are obtained in good yield by the action of potassium hydroxide on the following: 3-aldehydo-5-hydroxymethyl-*p*-cresol, 5-hydroxymethylsalicylaldehyde, 3-aldehydo-*p*-cresol, 5-aldehydo-*o*-cresol, and 3-aldehydo-*o*-cresol. [*Ber.*, 1930, 63B, 551-9; *Brit. Chem. Abst.*, 1930, 597A.] Claude describes the manufacture of hydrogen for high-pressure processes. [*Oesterr. Chem.-Ztg.*, 1930, 33, 64-5; *Chem. Abst.*, 1930, 3328.]

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